

We live immersed in an atmospheric sea of 79% nitrogen (N), yet N is the nutrient that most often limits biological productivity.

Nitrogen occurs in many forms in agricultural ecosystems because it can exist in a number of valence states within an ecosystem. The valence state in which nitrogen exists depends primarily on the ambient environment at micro-sites within the soil. The transformations and flow of nitrogen from one valence state to another constitute the basics of the nitrogen cycle ([Figure 8.1](#)). For example, atmospheric N_2 (0 charge) gas is converted by lightening to various oxides and finally to nitrate (+5 charge), which falls with the rain and is taken up by growing plants. Also N_2 gas can be converted to ammonia (-3 charge) by microbial fixation, with the NH_3 being used in various biochemical reactions within the plant. When plant residues decompose, much of the N they contain will undergo several microbial conversions and will eventually end up back as nitrates. Also under anaerobic conditions, nitrates can be reduced to various oxides and ultimately to N_2 gas again. Nitrogen in inputs such as fertilizers and manures is also subjected to these same microbial transformations. As indicated by [Figure 8.1](#), the N cycle is very complex and is influenced by many factors.

A global inventory of N in the biosphere shows that N is distributed in terrestrial, oceanic, and atmospheric components in the ratio 1:70:11818 ([Table 8.1](#)). Thus the bulk of the biospheric N is in the atmosphere. The atmospheric column on an hectare of land will contain approximately $8.4 \times 10^4 \text{ Mg ha}^{-1} \text{ N}$. Yet for growing most cereals and nonlegume forage crops, one has to apply large amounts of manure and/or fertilizer N. Nitrogen in soil originates from plant and animal residues, from fixation by leguminous plants and trees, and from components of rain such as nitrates ([Figure 8.1](#)). Total N content in the top 15 to 20 cm of surface soils ranges from 0.01% (or even less in desert soils) to more than 2.5% in peats. N content in the subsurface of any soil is generally less than in the surface layer since most organic residues are deposited on the soil surface. Under suitable conditions some of the organic nitrogen mineralizes into inorganic form and eventually may be present in ammonium (NH_4^+) and nitrate (NO_3^-) form.

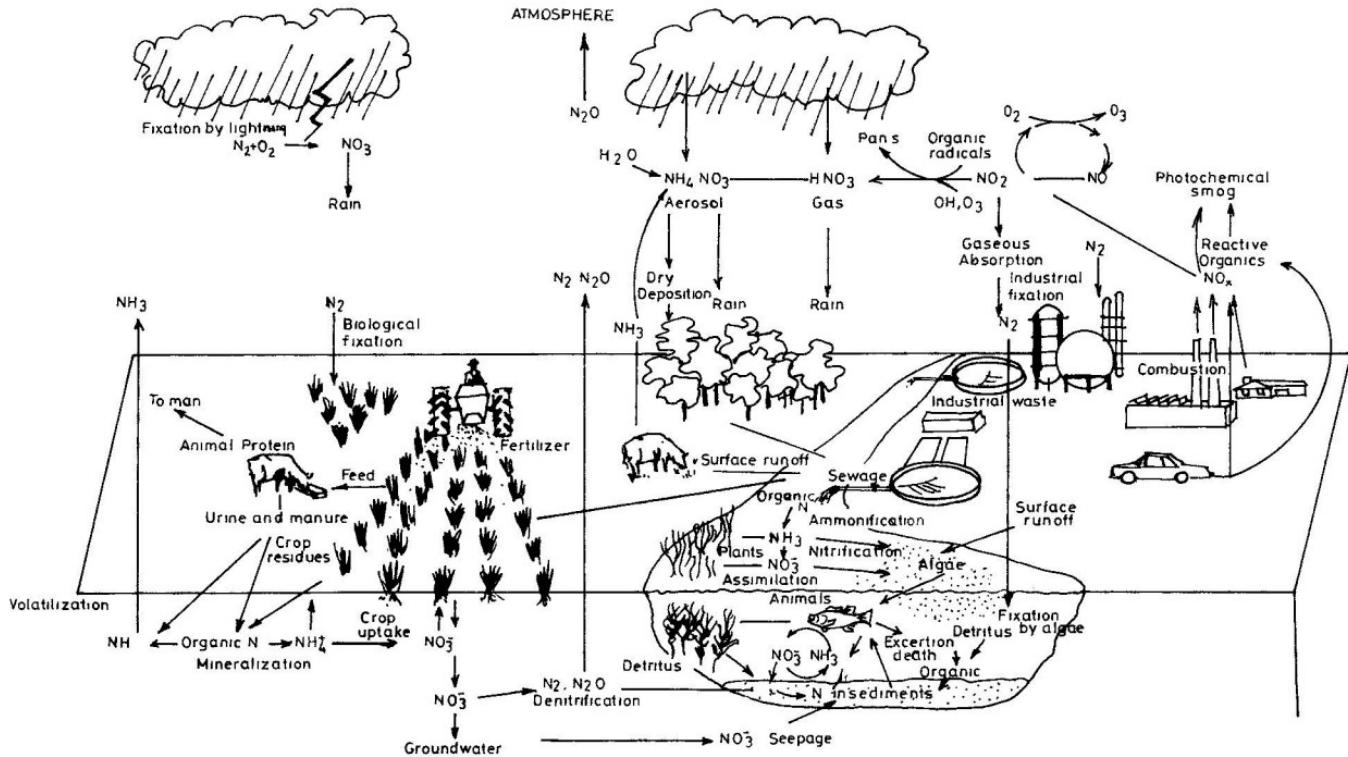


Figure 8.1. Schematic representation of the nitrogen cycle, emphasizing human activities that affect fluxes of nitrogen. (From NAS, 1978.)

**Table 8.1 Global Inventories of Nitrogen in the Biosphere
(Million Mg N)**

Terrestrial

Plant biomass	$1.1\text{--}1.4 \times 10^4$
Animal biomass	2×10^6
Litter	$1.9\text{--}3.3 \times 10^3$
Soil organic matter	3×10^6
Soil insoluble inorganic	1.6×10^6
Soil soluble inorganic	3×10^6
(Soil microorganism included in total soil organic matter)	5×10^6

Oceanic

Plant biomass	3×10^6
Animal biomass	1.7×10^6
Dissolved organic matter	5.3×10^6
Particulate organic matter	$0.3\text{--}2.4 \times 10^4$
N ₂ dissolved	2.2×10^6
N ₂ O dissolved	2×10^6
NO ₃ ⁻ dissolved	5.7×10^6
NO ₂ ⁻ dissolved	5×10^6
NH ₄ ⁺ dissolved	7×10^6

Atmospheric

N ₂	3.9×10^6
N ₂ O	1.3×10^6
NH ₃	0.9
NH ₄ ⁺	1.8
NO _x	1–4
NO ₃	0.5
Organic N	1

From Winteringham, F.P.W. 1980. *Soil N as Fertilizer or Pollutant*. With permission of IAEA.

However, inorganic N in soil at any moment is only a small fraction of total soil N. The bulk of soil N in a surface soil is present in the organic form. In fields where chemical fertilizer is not applied, nonleguminous crop plants obtain most of their nitrogen from soil organic N after its mobilization. In subsoils (especially those with illitic clays) much of the nitrogen present is trapped in the clay lattice as nonexchangeable ammonium and is largely unavailable for plant uptake.

8.1. SOIL ORGANIC N

Soil organic N consists of proteins (20 to 40%), amino sugars such as the hexosamines (5 to 10%), purine and pyrimidine derivatives (1% or less), and complex unidentified compounds formed by reaction of ammonium with lignin, polymerization of quinones with nitrogen compounds, and condensation of sugars and amines. Some of these have already been discussed in the chapter on organic matter. Part of the organic N is also present as clay-humus complexes, which are resistant to decomposition. This would also explain why only a very small part of immobilized fertilizer N becomes available to the growing crop plants.

8.2. MINERALIZATION OF SOIL ORGANIC NITROGEN

Mineralization of soil organic nitrogen is the microbial process by which organic forms of N in soils are converted to inorganic forms (ammonium, nitrite, and nitrate). Mineralization takes place in three step-by-step reactions, namely, aminization, ammonification, and nitrification. Of these three reactions, the first two are carried out by heterotrophic microorganisms, while the third one is carried out by autotrophic bacteria. Heterotrophs derive their energy from oxidation of organic carbon compounds, while autotrophs obtain their energy from specific inorganic salts and their carbon from bicarbonate salts in the soil. Organic N in soils is ultimately derived from decomposition of plant material returned to the soil. This organic N may be present in both relatively labile forms (crop residues and microbial biomass) and in organic compounds more resistant to decomposition (lignoproteins, various types of humates, and condensed cyclic molecules).

8.2.1. Aminization

The heterotrophs, including bacteria, fungi, and actinomycetes, break down complex organic molecules releasing amines and amino acids; this process is known as aminization. Bacteria and actinomycetes often dominate in neutral and alkaline conditions, while fungi are more active under acid conditions. Most N undergoing aminization during a growing season originates from degradation of proteins and amino acids in decomposing crop residues and microbial cells, with lesser amounts originating from decomposition of the more resistant sources such as lignoproteins and humates.

8.2.2. Ammonification

Ammonification consists of the biological processes by which organic forms of soil nitrogen are converted to ammonia or ammonium ions. The final reaction in these processes is the hydrolysis of amino groups. The amines and amino acids released in aminization are reacted upon by other heterotrophs,

which release N in the inorganic NH_4^+ form. Both aerobic and anaerobic microorganisms are capable of carrying out this reaction. Also a very diverse population of bacteria, fungi, and actinomycetes is capable of releasing ammonium. The ammonium released may be

1. Lost by ammonia volatilization
2. Utilized by plants
3. Absorbed on the exchange complex of clay minerals
4. Fixed in the crystal lattice of 2:1 expanding clay minerals
5. Immobilized by soil microorganisms
6. Nitrified

Ammonification can occur in both aerobic and anaerobic environments, although rates are generally more rapid in the aerobic environment.

8.2.3. Nitrification

This is a two-step process. In the first step ammonium is converted to nitrite (NO_2^-), and in the second step nitrite is converted to nitrate (NO_3^-). A group of obligate autotrophic bacteria known as *Nitrosomonas* is responsible for the first step, that is, conversion of ammonium to nitrite. Conversion of nitrite to nitrate is carried out by another group of obligate autotrophic bacteria known as *Nitrobacter*. It should be mentioned that, although *Nitrosomonas* and *Nitrobacter* are the most important organisms responsible for the reactions mentioned above, a few heterotrophs can also carry out these reactions, usually at much lower rates. Nitrates so formed may be

1. Taken up by plants.
2. Lost by leaching — creating health hazards by increasing nitrate concentration in underground water.
3. Under anaerobic conditions lost by denitrification — creating atmospheric pollution problems. Nitrous oxide (N_2O), one of the products of denitrification, is involved in depletion of the ozone layer.
4. Immobilized by soil microorganisms.

8.3. FACTORS AFFECTING NITRIFICATION

With the exception of rice most of our agricultural production is from well-drained soils, which favor nitrification. Nitrates therefore dominate as the form in which inorganic N is present in soil. A major exception is land continuously under perennial grasses where ammonium may be present in larger amounts. Therefore most crop plants have developed to utilize nitrate (NO_3^-) as a major source of N. In recent years, however, considerable evidence has accumulated to show that even upland plants grow better when a mixture of ammonium NH_4^+ and nitrate NO_3^- are present.

It is obvious that the factors that have a pronounced effect on the activity of nitrifying bacteria will affect nitrification. Some of these factors are soil water content, aeration, pH, temperature, supply of ammonium, and population of nitrifying organisms.

8.3.1. Soil Water and Aeration

Nitrification is brisk in soils having adequate soil water and air; in most soils this is near field capacity. Data on the effect of soil water potential on nitrification, as reported by Mahli and McGill (1982), are given in [Table 8.2](#). At a water potential of 0 K Pa, that is, saturation, there is little or no air in soil pores, and nitrification completely ceases (100% water-filled pore space). In well-aerated soils nitrification increases as the water content increases from 1.5 M Pa (megapascal) potential (permanent wilting point) to -33 kPa (or -0.033 M Pa) (near field capacity), nitrification being greatest near field capacity. Again, data in Table 8.2 also indicate that at the same soil water potential, nitrification rate increased as soil clay content decreased (from silty clay loam to sandy loam). The latter soil had lesser water content and therefore better aeration. These relationships between soil water content and rates of aerobic microbial activity (such as nitrification) were shown graphically by Linn and Doran (1984) where soil water content was expressed as percent water-filled pore space (percent saturation). They found that ammonification and nitrification for the soils studied was maximum near 60% water-filled pore space, which corresponds closely to field capacity ([Figure 8.2](#)). Ammonification results from activity of many microbial species, both fungal and bacterial. However, nitrification is specific for a small group of bacteria. These bacteria are obligate aerobes and are more sensitive to water stress than some of the soil fungi. Consequently, as a soil becomes dry, often soil ammonium accumulates because ammonification proceeds more rapidly than nitrification.

8.3.2. Soil pH

Morrill and Dawson (1967) studied nitrification in 116 soils of the United States ranging in pH from 4.4 to 8.8 and observed four different patterns, which are as follows:

1. In some acid soils having $\text{pH} < 5.39$, NH_4^+ oxidized slowly to NO_3^- without the appearance of NO_2^- .

* Water content in soil when, after saturation, it is allowed to drain under gravitational pull until percolation ceases; this state may be reached at a soil water potential of -33 K Pa (or -0.033 M Pa) in medium- to heavy-textured soils to 0 to 10 K Pa (or -0.01 M Pa) in light, sandy soils. Also in dry soils ammonium and sometimes nitrite may accumulate, presumably because *Nitrobacter* is more sensitive to water stress than other microbes.

Table 8.2 Effect of Soil Water Potential on Nitrification in Three Canadian Soils

Soil water potential (KPa)	Period of incubation (days)	Rate of nitrification ($\mu\text{g N g}^{-1} \text{ day}^{-1}$)		
		Cooking Lake	Falun	Malmo
0	8	0.0 d ^a	0.0 d	0.0
-33	8	3.6 a	3.4 a	3.2 a
-700	11	2.0 b	2.1 b	2.0 b
-1500	17	1.3 c	1.3 c	1.2 c

Note: Cooking Lake is gray luvisol sandy loam; Falun is dark gray chernozemic loam; and Malmo is black chernozemic clay loam.

- ^a In each column, the values are significantly different (95% level of probability) when not followed by the same letter.
- ^b Water content at -33 KPa in Cooking Lake, Falun, and Malmo was 15.5, 20.7, and 39.7%, respectively.

From Malhi and McGill, 1982. *Soil Biol. Biochem.* 14:393–399. With permission of Pergamon Press.

2. In some acid soils having $\text{pH} \leq 5.39$, there was accumulation of NH_4^+ with very little oxidation to NO_2^- and NO_3^- .
3. In soils having $\text{pH} 5.01$ to 6.38 , NH_4^+ and NO_2^- are rapidly oxidized to NO_3^- .
4. In soils having $\text{pH} 6.93$ to 7.85 , NH_4^+ oxidized to NO_2^- , which accumulated for extended periods before being oxidized to NO_3^- .

They also observed that on liming acid soil patterns “1” and “2” identified above changed to pattern “3.” In another study (Dancer et al., 1973) observed a linear relationship between the soil pH range of 4.7 to 6.4 and nitrification (Figure 8.3). Effects of liming to obtain a desired pH confirmed this relationship (Figure 8.4).

Studies involving still wider pH ranges suggest a pH optimum for nitrate formation between pH 6.0 and 9.4. Nitrification can continue even when pH is greater than 9.4. Nitrite oxidation may be inhibited more than ammonium oxidation at high pH values, sometimes resulting in accumulation of nitrites.

Nitrification of both soil and fertilizer nitrogen releases H^+ ions as shown in the reaction below:



Nitrification is thus an acid-producing process per se, and continuous use of ammonium or ammonium-producing fertilizers or even heavy dressings of organic manures result in lowering the soil pH. (See also Chapter 6 on soil acidity.)

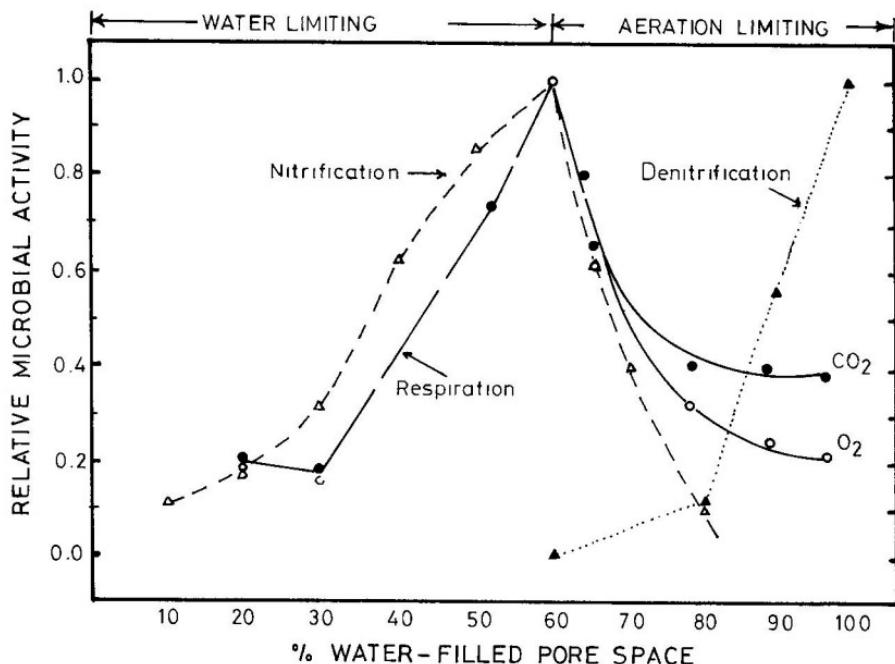


Figure 8.2. The relationship between water-filled pore space and relative amount of microbial nitrification (after Greaves and Carter, 1920), denitrification (after Nommiik, 1956), and respiration (O_2 uptake, s-s, CO_2 production, d-d) (Linn and Doran study). Data for nitrification originally expressed as percentage water-holding capacity. (From Linn and Doran, 1984. Soil Sci. Soc. Am. J. 40:1267–1272. With permission of SSSA.)

8.3.3. Soil Temperature

Soil temperature as a factor controlling nitrification has been a matter of concern in cooler climates, since the availability of native soil N depends very much on nitrification. Soils in cooler climates have, in general, much more organic matter than soils in warmer climates. Therefore the contribution of native soil N toward crop production could be substantial in cooler regions, with nitrification values of over 200 kg N ha^{-1} being reported for some growing seasons.

The optimum temperature for nitrification in temperate soils is between 25 and 35°C (Sabey et al., 1959). However, Malhi and McGill (1982) from Canada reported an optimum of 20°C , while Schloesing and Muntz (1879) reported the optimum temperature for nitrification to be 37°C , with the process continuing to 46 to 50°C and ceasing at 55°C . The effect of temperature on nitrification varies with the climate, and this seems to be well supported when comparing data of Malhi and McGill (1982), Myers (1975), and Sabey et al. (1959) (Figure 8.5). Thus there is a climatic selection of species of nitrifiers,

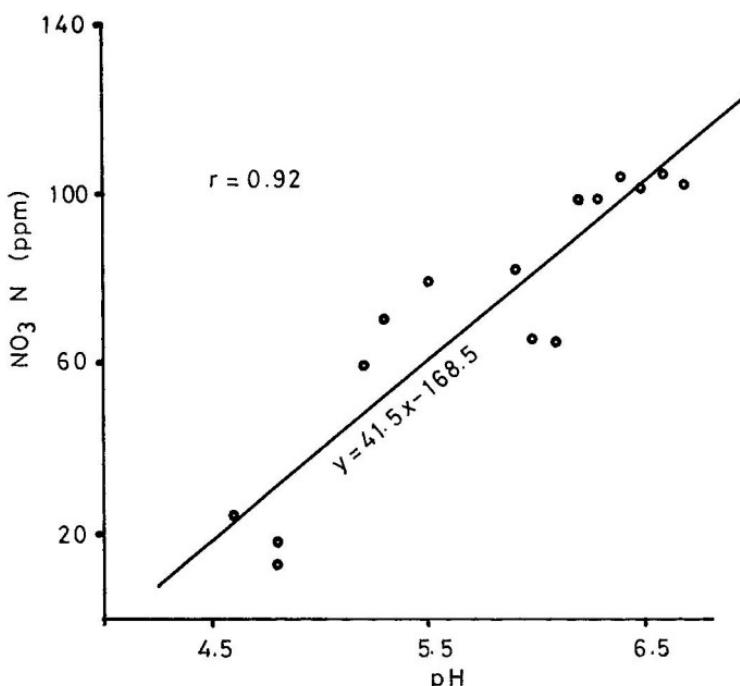


Figure 8.3. Relation between soil pH and NO₃⁻-N accumulation in soils treated with 100 ppm of NH₄⁺-N as (NH₄)₂SO₄ and incubated for 15 days at 23°C. (From Dancer et al., 1973. Soil Sci. Am. Proc. 31:67–69. With permission of SSSA.)

with those from cooler climates having lower temperature optima and less heat tolerance than species from warmer regions.

Nitrification has been shown to proceed even at 0°C (Eggleton, 1935). Thus nitrifying bacteria appear to be resistant to freezing at least in natural environments, as nitrification may be rapid when frozen soils thaw. Nitrates may also be redistributed in soil profile by internal drainage after thaw.

8.3.4. Supply of Ammonium

Since ammonium is the substrate that is nitrified, an adequate supply is essential for nitrification. Factors such as ammonia volatilization loss reduce the amount of ammonium and thereby the amount of nitrates formed. Similarly, rapid immobilization of ammonium by soil microorganisms, especially when organic residues with wide C:N ratio are incorporated, will also reduce nitrification.

Very high ammonium concentrations may retard nitrification; the maximum tolerable amounts could be as high as 800 µg g⁻¹ soil. The depressing effect of high concentrations of ammonium may be attributed to toxic levels of ammonia, salt effects, or to lowering of pH when ammonium sulfate is added as a source of N. Because of the toxic effect of high NH₄⁺ concentrations, application of

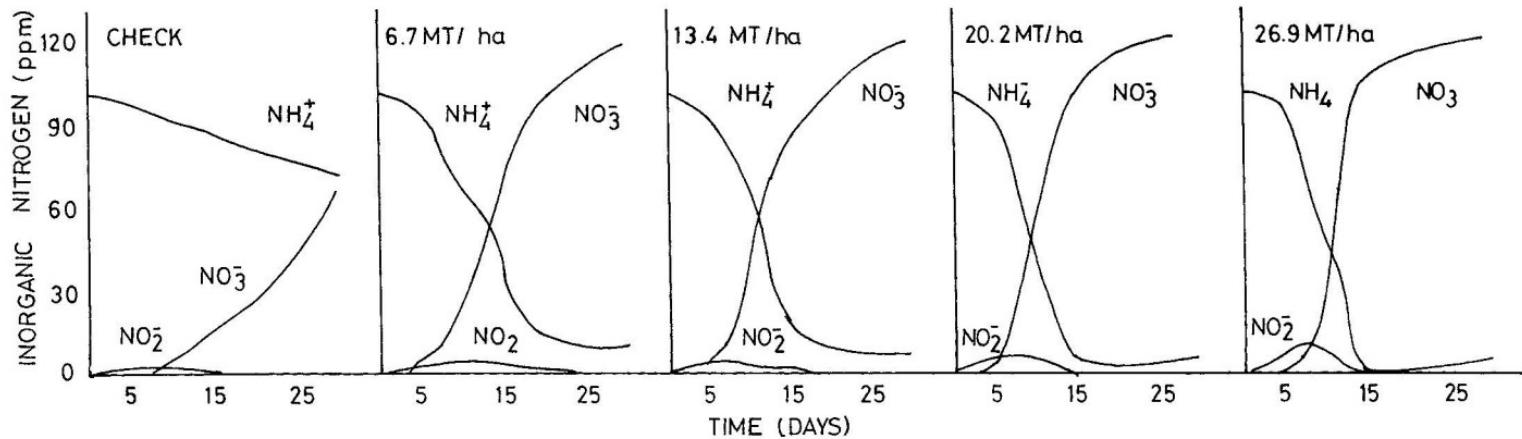


Figure 8.4. Effect of liming and soil pH on the concentration of NH_4^+ , NO_2^- and NO_3^- -N in soil treated with 100 ppm of NH_4^+ -N as $(\text{NH}_4)_2\text{SO}_4$ and incubated for 30 days at 23°C. Treatments 0, 6.7, 13.4, 20.2, and 26.9 metric tons ha^{-1} of lime correspond to pH values of 4.7, 5.3, 6.0, 6.3, and 6.6, respectively. (From Dancer et al., 1973. Soil Sci. Soc. Am. Proc. 31:67–69. With permission of SSSA.)

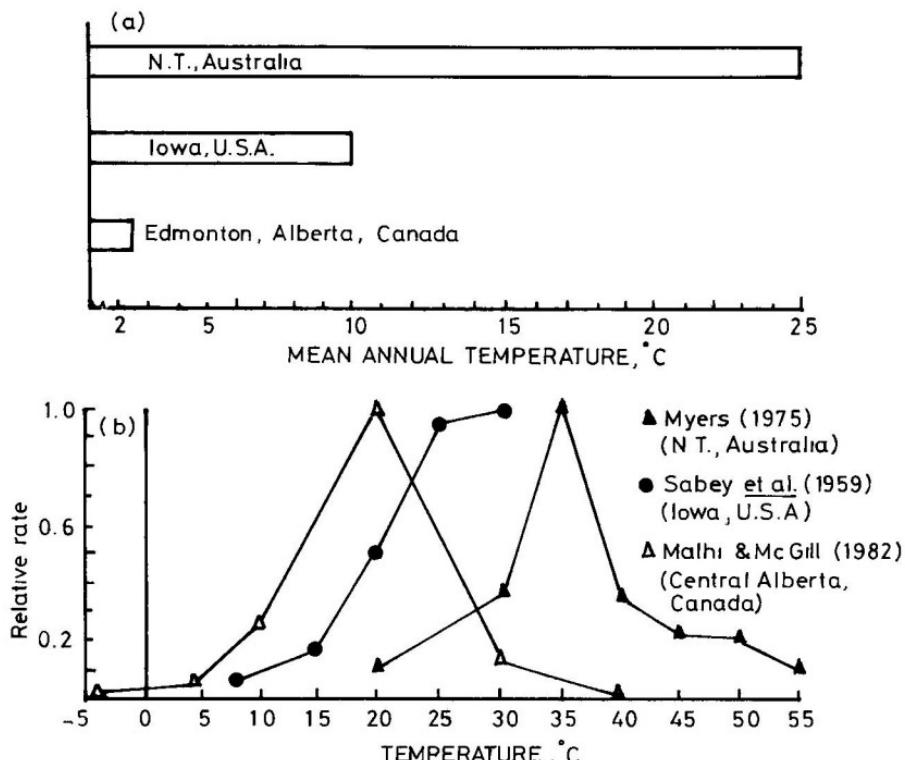


Figure 8.5. The effect of soil temperature on relative nitrification rate at Edmonton compared with published results from two warmer climatic regions: (a) Mean annual temperature for the three locations and (b) Relative nitrification rates. (From Malhi and McGill, 1982. *Soil Biol. Biochem.* 14:393–399. With permission from Elsevier Science Ltd.)

anhydrous ammonia results in temporary sterilization of the soil in and near the band. The ammonium ions must diffuse out of the band to be nitrified.

8.3.5. Population of Nitrifying Organisms

Population of nitrifying organisms in soils is the most important factor in determining rate of nitrification. Factors affecting nitrification discussed above exert their influence primarily through their effects on the population of nitrifying organisms in soil. Nitrifying organisms are essentially universally present in surface soils. However, beneath the zone of weathering, the ambient habitat supports few if any nitrifiers. Population and activity of nitrifying organisms in surface soils can be reduced by use of nitrification inhibitors. For example, by measuring the accumulation of nitrite-N in soil following application of the nitrification inhibitors nitrapyrin, dicyandiamide, and thiourea, Zacherl and Amberger (1990) showed that these materials reduced growth of *Nitrosomonas europea* (Figure 8.6).

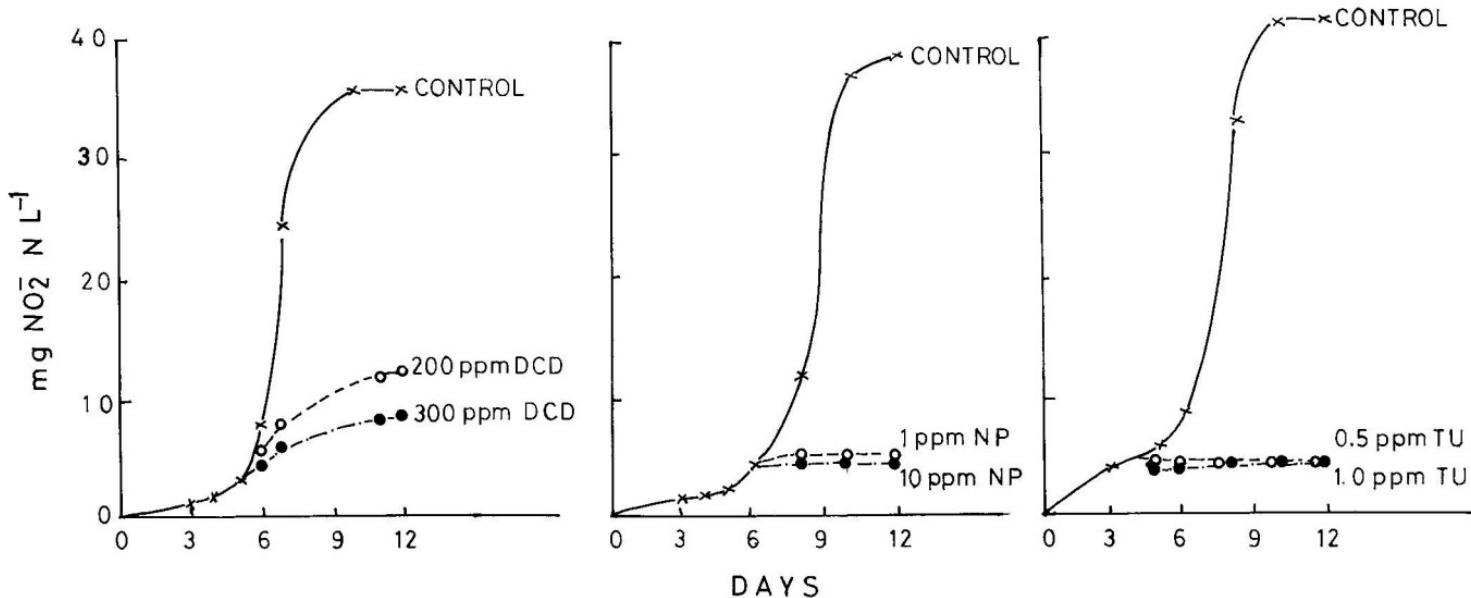


Figure 8.6. Effect of dicyandiamide (DCD), nitrappyrin (NP), and thiourea (TU) on the growth of *Nitrosomonas europea* in pure culture. (From Zacheri and Amberger, 1990. *Fert. Res.* 22:37–44. With permission of Kluwer Academic.)

8.4. NITROGEN IMMOBILIZATION

Nitrogen immobilization occurs when inorganic soil N is converted to organic forms through biological activity. Immobilization of soil or fertilizer nitrogen occurs when large quantities of carbon-rich materials (i.e., low-nitrogen crop residues such as cereal straw, sugars, alcohol) are applied to soil. Results from a field study in which ^{15}N urea was applied to rice at 60 or 120 kg N ha $^{-1}$ in a rice-wheat double cropping system showed that about 16.7 to 25.6% of applied N remained in the soil after harvest in immobilized organic forms (Goswami et al., 1988). Data from field experiments with ^{15}N show that more inorganic N was immobilized with NH $_4^+$ than with NO $_3^-$ fertilizers (Powlson et al., 1986). Laboratory studies confirm that when both NH $_4^+$ and NO $_3^-$ forms of N are available, the soil microorganisms selectively immobilize NO $_3^-$ only after NH $_4^+$ -N was nearly exhausted (Figure 8.7) (Recous and Mary, 1990). This occurs because the quantity of energy (soluble C) needed to incorporate one unit of N into plant protein is greater with nitrate than with ammonium. This results from the fact that nitrate-N must first be reduced to the 3 $^+$ valence state within plant cells before it can be utilized in protein synthesis. Thus appreciable nitrate immobilization will take place only when large amounts of C are available.

8.5. AMMONIUM FIXATION (NONEXCHANGEABLE AMMONIUM)

Fixed ammonium is the ammonium held between the lattice of 2:1 expanding clays (illites, montmorillonites, etc.), particularly in illitic soils. This ammonium is generally not affected by cations on the clay surface and is not removed with KCl solution. However, near the edges of clay lattice, external ions may replace some of this ammonium if clays are expanded, and such nitrogen may become available for plant growth. Much of the literature available relates to the ammonium held near the edges of the clay lattices.

The ionic radius of NH $_4^+$ ion is 1.48 Å, which is close to that of K $^+$ (1.33 Å), and therefore NH $_4^+$ ions can also be fixed in the interlayer spaces of expanded lattices of clay minerals. For this reason the addition of potassium fertilizer before application of ammonium or ammonium-producing fertilizers can reduce ammonium fixation. Fixed ammonium ions near the edge of clay lattices can be replaced by cations that expand the lattice (Ca $^{2+}$, Mg $^{2+}$, Na $^+$, H $^+$), but not by those that contract it K $^+$, Rb $^+$, Cs $^+$.

In the rice-producing montmorillonitic Beaumont soils of Texas (Chen et al., 1989), fixed ammonium may make a major contribution toward N supply to rice. In general, native ammonium fixed within the clay lattice is not available, while that held near the edge of the clay lattice only gradually becomes available to crops over years (Black and Waring, 1972).

Most ammonium fixation occurs in the clay fraction of the soil, while some may occur in the silt fraction. Very good correlation between clay content

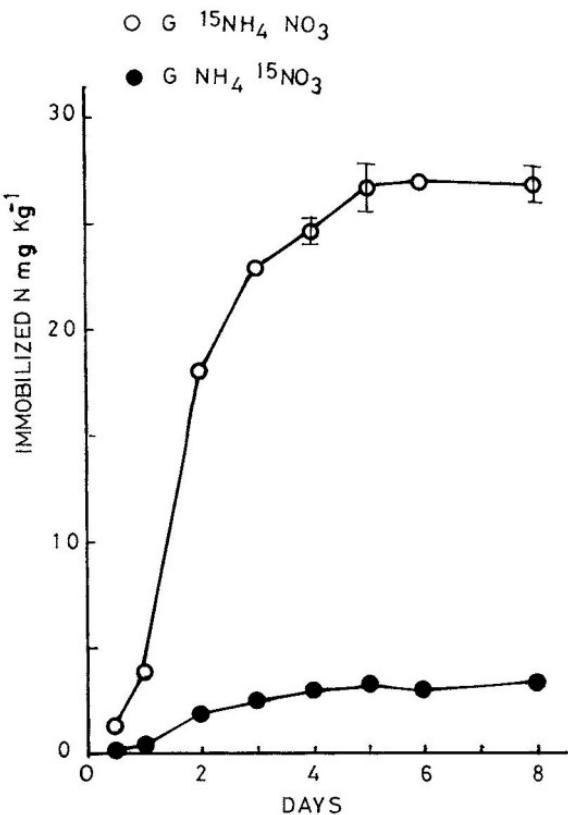


Figure 8.7. Immobilization of N in a loamy soil (soil I) incubated at 10°C with 500 mg C-glucose kg^{-1} soil, 100 mg N kg^{-1} soil applied as $^{15}\text{NH}_4\text{NO}_3$ or $\text{NH}_4^{15}\text{NO}_3$. Values are the mean of two replications. (From Recous and Mary, 1990. Soil Biol. Biochem. 22:913–922. With permission from Elsevier Science Ltd.)

and fixed ammonium has been reported (Sparks et al., 1979; Jensen et al., 1989). Jensen et al. (1989) separated clay and silt fractions of soil by ultrasonic technique and showed that in four Danish soils fixed ammonium in the clay fraction varied from 255 to 430 $\mu\text{g N g}^{-1}$, while that in the silt fraction varied from 72 to 166 $\mu\text{g N g}^{-1}$. Similarly, for a Canadian soil with 37% clay, Kowalenko and Ross (1980) reported values of 335 $\mu\text{g g}^{-1}$ for clay and 8.3 $\mu\text{g g}^{-1}$ for silt.

In addition to clay minerals, soil organic matter can also fix NH_4^+ in nonexchangeable forms. Also NH_4 -organic matter complexes are extremely resistant to microbial decomposition. Aromatic compounds and their unsaturated alicyclic counterparts are primarily responsible for NH_4 -fixation by soil organic matter. Mechanisms responsible for ammonium fixation by soil organic matter are not yet well understood.

In addition to clay type and content, important factors affecting ammonium fixation in soil are (1) amount of ammonium added; (2) soil water

content, drying, and wetting; (3) presence of other ions (especially K^+); and (4) freezing and thawing.

The amount of ammonium fixed in the edges of clay lattices generally increases with increasing amounts of ammonium added.

Soil water content affects ammonium fixation because clay particles remain expanded in moist soils and fixation is reduced. On drying, the inter-layer spaces in the clay and minerals contract, trapping ammonium ions that have diffused into the edges of the lattice. In a clayey soil at 60% of maximum water-holding capacity, NH_4^+ fixation was one-fourth that for the dry soil (Osborne, 1976).

Regarding the presence of other ions, a study by Chen et al. (1989) showed that saturation of Beaumont and Lake Charles soils with Ca reduced fixation of added ammonium and resulted in release of fixed ammonium (Figure 8.8); ^{15}N data showed that this release was from the chemically added fraction and not from the indigenous (interior) fixed ammonium. Typically, K^+ and NH_4^+ ions in the external solution cause the lattices of 2:1 clay to collapse, restricting diffusion into and out of the edges of clay particles. On the other hand, larger cations (especially Na^+ because of its hydration) expand the lattices and allow more diffusion and exchange to occur.

Regarding anions, the presence of phosphate may increase ammonium fixation. Mandal and Mukhopadhyay (1984) reported 980 to 1134 mg kg^{-1} soil NH_4^+-N fixation with DAP as compared with 910 to 1097 mg kg^{-1} soil with ammonium sulfate in three soils of West Bengal, India.

Since freezing removes water from the system, it may influence the amount of ammonium fixed. For example, Walsh and Murdock (1960) showed that a treatment for 5 days at $-15^\circ C$ increased NH_4^+ fixation in a number of podzolic soils from 0.08 to 0.14 cmol kg^{-1} of soil.

8.6. NH_4^+ VERSUS NO_3^- NUTRITION OF PLANTS

Theoretically, NH_4^+ should be the preferred form of N since it does not need to be reduced before incorporation into organic materials. However, in most well-drained soils suitable for crop production, oxidation of NH_4^+ to NO_3^- is fairly rapid, and therefore most plants growing under well-drained conditions have developed to grow better with NO_3^- . In recent years there has been increased interest in NH_4^+ versus NO_3^- nutrition of crops, and the results of a number of studies indicate better growth of plants and higher yield with a mixture of NH_4^+ and NO_3^- rather than a single ionic form (Hageman, 1984). The availability of nitrification inhibitors (chemicals that inhibit or retard nitrification) has permitted maintaining higher concentrations of ammonium for longer periods in fields (Joseph and Prasad, 1993). For wheat and many other crops, NH_4^+ to NO_3^- ratios of 50:50 and 75:25 appear to be near optimum. With coarse-textured soils, especially when they are slightly alkaline, an enhanced NH_4^+ regime may be advantageous for the growth of corn. Thus for

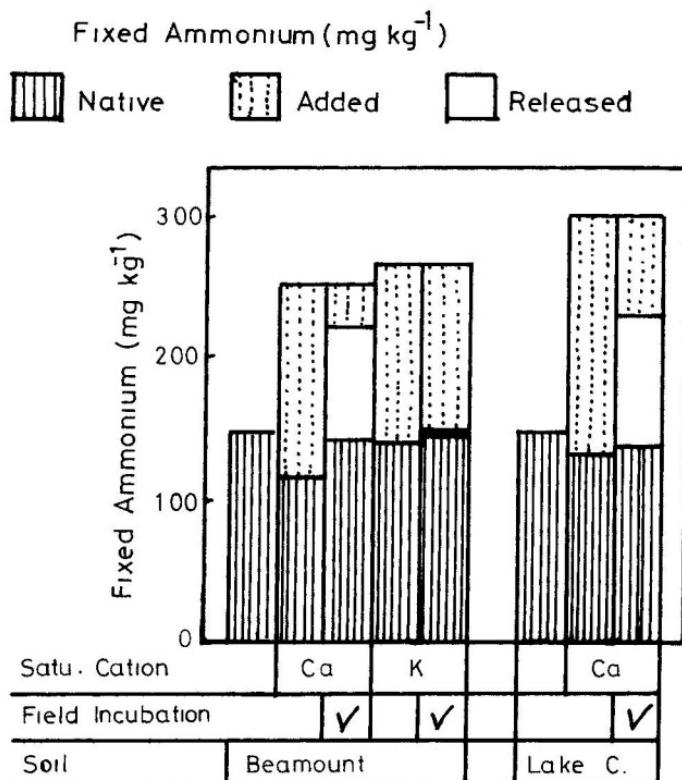


Figure 8.8. Native and added fixed NH_4^+ as influenced by chemical treatment and field incubation in Beaumont and Lake Charles soils. (From Chen et al., 1989. *Soil Sci. Am. J.* 53:1039. With permission of SSSA.)

crops growing on well-drained soils, a mixed availability of NH_4^+ and NO_3^- nitrogen is considered ideal.

Rice, which grows under submerged soil conditions, must feed mostly on NH_4^+ because NO_3^- is not stable under those conditions. Nitrates under submerged conditions are lost by denitrification (discussed later in this chapter). The term amoniphilic (ammonia-loving) plants has been suggested for plants such as rice that feed on NH_4^+ (Prasad et al., 1983). When urea is used as fertilizer, rice plants may also absorb some directly as molecular urea (Mitsui and Kurihara, 1962; Saraswathi et al., 1991).

8.7. BIOLOGICAL NITROGEN FIXATION

Nitrogen-fixing organisms can be broadly classified into those that are free-living and those living in association with plants. Nutman (1971) has made a fairly detailed listing of N-fixers of both groups. Total global biological nitrogen fixation by all the different types of organisms is estimated to be

Table 8.3 Global Rates of Nitrogen Fixation

Process	Amounts (million Mg yr ⁻¹)
Terrestrial biofixation	
Legumes	36
Rice paddies	4
Other crops	5
Grasslands ^a	45
Forests ^a	40
Others	10
Total	140
Oceanic biofixation	20–120
Industrial fixation (including fertilizers)	89
Terrestrial combustion processes	19

^a Would also include legumes.

From Winteringham, 1980. *Soil N as Fertilizer or Pollutant*. With permission of IAEA.

approximately 175 million Mg yr⁻¹, of which legumes alone account for almost half (80×10^6 Mg). Estimates of global fixation and losses of N by different sources are given in Table 8.3, while N-fixation in kg⁻¹ ha⁻¹ year by selected organisms or systems are given in Table 8.4. A list of nitrogen-fixing organisms and associations is given in Table 8.5.

Although the overall process $N_2 \rightarrow 2 NH_3$ is exergonic (-104 kJ/mole), high energy input (940 kJ/mole) is required to rupture the $N \equiv N$ bond. Thus, whatever the source, the manufacture of nitrogen fertilizer is highly energy dependent. Recent interest in biological N_2 -fixation and biofertilizers (Verma, 1993) is due to the fact that biological fixation uses solar energy, the most inexhaustible energy source, for producing ammonia from nitrogen for use in the protoplasm of organisms.

8.7.1. Nitrogen Fixation by Legumes

Rhizobium species of bacteria living in a symbiotic relationship in root nodules of legumes are capable of converting atmospheric N_2 gas to NH_3 . NH_3 is then utilized by the legume to form amino acids and proteins. The rhizobia obtain the energy needed for their growth and for the fixation of N ultimately from products of photosynthesis formed in the legume. By some estimates, this can be as much as 35% of the energy fixed by photosynthesis. For this reason, seldom is biomass production by an N-fixing legume as great as that of cereal crops, when no other factors limit growth.

Table 8.4 Biological Nitrogen Fixation by Different Organisms/Systems

Organism or system	N-fixed (kg ha ⁻¹ yr ⁻¹)
Legumes	
Forage	57–700
Grain	17–270
Nodulated nonlegumes	
<i>Alnus</i>	40–300
<i>Hippophae</i>	2–179
<i>Ceanothus</i>	60
<i>Coriaria</i>	150
Plant algal associations	
<i>Gunnera</i>	12–21
<i>Azollas</i>	31
Lichens	39–84
Free-living microorganisms	
Blue green algae	25
<i>Azotobacter</i>	0.3
<i>Clostridium pasteurianum</i>	0.1–0.5

From Nutman (1971) and Evans and Barber (1977).

Although the causative organism responsible for nitrogen fixation in pure culture was isolated by Beijerinck in 1888 (Waksman, 1952), growing legumes to maintain and build up soil fertility has been practiced since ancient times. It is now well established that the enzyme nitrogenase is involved in nitrogen fixation both in free-living organisms and those living in associations. The nitrogenase enzyme complex in combination with the necessary reactants catalyzes the reduction of nitrogen to ammonia. This enzyme complex consists of two protein components. The first is a larger molybdenum-iron protein having a molecular weight of 2 to 2.7×10^5 and containing one or two atoms of molybdenum, 17 to 36 iron atoms, and 14 to 28 acid labile sulfur atoms per protein molecule. The second is an iron-protein molecule having a molecular weight of 55 to 67×10^3 and containing four atoms each of iron and acid-labile sulfur per protein molecule (Evans and Barber, 1977).

There is no doubt a specificity exists between *Rhizobium* strain and the legume, and compatibility between the two is essential for successful nodulation. This necessitates using specific cultures for different legumes; when growing a new legume species on a soil, it is necessary that the appropriate *Rhizobium* culture be applied. The benefit of seed inoculation with specific *Rhizobial* cultures has been proved the world over.

There is considerable variation in nitrogen fixation by different legumes. Perennial legumes cut for forage generally fix more than 100 kg N ha⁻¹,

Table 8.5 Nitrogen-Fixing Organisms and Associations

Kind of organisms	Examples
Free-living organisms	
Photosynthetic bacteria	<i>Rhodospirillum, Chromatium, Chlorobium</i>
Aerobic bacteria	<i>Azotobacter, Beijerinckia, Derxia,</i>
	<i>Spirillum, Thiobacillus</i>
Facultative bacteria	<i>Klebsiella, Bacillus, Vibrio</i> (methane oxidizers)
Obligate anaerobic bacteria	<i>Clostridium, Methanobacterium, Desulfovibrio</i>
Actinomycetes	<i>Mycobacterium, Nocardia, Actinomyces</i>
Blue-green algae	
Heterocystous	<i>Anabaena, Aphanizomenon, Gloeotrichia, Nostoc, Calothrix, Shizothrix</i>
Nonheterocystous	<i>Gloeocapsa, Oscillatoria, Plectonema</i>
Nonobligatory Associations ^a	
Animal associations (bacteria)	Termites, sea urchins, cattle sheep
(blue-green algae)	<i>Azolla</i> (<i>Anabaena</i>): <i>Sargassum</i> (<i>Dichothrix</i> , blue-green algae); <i>Codium</i> , a macro-green alga, <i>Azotobacter</i>
Leaf surfaces of angiosperms (bacteria)	Various tropical plants
Leaf nodules (bacteria)	<i>Psychotria</i> , a tropical plant (<i>Klebsiella</i>)
Lichens (blue-green algae and fungi)	<i>Peltigera aphthosa</i> (<i>Nostoc</i>)
Root nodules of tropical gymnosperms (blue-green algae)	<i>Podocarpus, Macrozamia, Cycas</i>
Obligatory symbioses	
Nonleguminous angiosperms (root nodules)	Alder tree — <i>Alnus</i> sp., <i>Myrica, Elaeagnus, Coriaria, Dryas</i>
Legume root nodules (<i>Rhizobium</i> spp.)	Beans, peas, alfalfa, clover, soybeans, lentils

^a Nitrogen-fixing agent in parentheses.

Modified from Burns and Hardy (1975).

sometimes as much as 400 to 600 kg N ha⁻¹. Both temperate and tropical species are equally effective. As compared with forage legumes, grain legumes fix appreciably less (Table 8.6) because of their shorter growing season and because the nitrogen left in the haulm is usually not recorded. Intercropping systems in which a grain legume is grown between widely spaced cereal crop rows (such as maize, sorghum, millet, cotton, and sugarcane) are being developed. These intercropping systems permit the production of grain legumes as a bonus crop, thereby providing bonus nitrogen fixation. In some of these

Table 8.6 Nitrogen Fixed by Different Legumes

Legumes	kg N ha ⁻¹ yr ⁻¹
Forage Legumes	
Temperate	
Clovers	23–620
Lucerne	164–300
Tropical	
Stylo	30–196
Tick clover	700
Grain Legumes	
Temperate	
Vetch and tick beans	57–190
Peas	46
Lupins	128
Tropical	
Lentil	35–77
Pigeonpea	41–150
Cowpea	73–354
Soybean	17–206
Cluster beans	37–196
Groundnut	33–111
Chickpea	41–270
Mung beans	224

From Nutman, 1971. Sci. Prog. Oxford 59:55–74. With permission of Science Reviews Ltd., Middlesex, England.

experiments additional yields of the main crop have been reported, suggesting some transfer of nitrogen from the companion legume crop. Also, multiple and relay-cropping systems have been developed with a legume crop as a component.

The practice of growing legumes to a certain vegetative stage and then incorporating them into the soil is known as “green manuring” and is another way of utilizing biological N fixation *in situ*. A large number of crops and species have been used as green manure including sunnhemp (*Crotolaria juncea* L.), dhaincha (*Sesbania aculeata* [wild] Poir), Phillipasera (*Phaseodru trilobus* Ait), mung bean (*Vigna aureus* L.), cowpea (*Vigna aculeata*), cluster beans (*Cyamopsis tetragonoloba* L.), senji (*Melilotus alba* Medik.), and khesari (*Lathyrus sativus*). In some regions green matter from leguminous and nonleguminous plants may be added as green manure. The tree species and other plants used include *Thespesia populnea* L., *Cassia Auriculata* L., *Pongamia glabra* Vent., *Azadirachta indica* A. Juss., *Calotropis gigantea*, *Jatropha*

gossypifolia L., *Jatropha glanduliflora* Roxb., *Gliricidia maculata* (H.B. and K.) *Tephrosia purpurea* L., *Tephrosia candida* (Roxb) DC., *Cassia tora* L., and *Ipomea carnea* auct. (non-Jacq.).

Likewise, in temperate regions a number of legume species are used as green manures. For cool season plantings, especially if growth is to be terminated within 40 to 70 days, species such as field peas (*Pisum sativum* L.), faba bean (*Vicia faba* L.), hairy vetch (*Vicia villosa* Roth subsp. *villosa*), black medic (*Medicago lupulina* L.), lentils (*Lens culinaris*, Medikus), and crimson clover (*Trifolium incarnatum* L.) are often used. For warmer season plantings some of the above species plus soybean (*Glycine max* L. Merr.), flatpea (*Lathyrus sativus* L.), and tinga pea (*Lathyrus tingitanus* L.) are possible selections. In hot seasons many of the species listed above for the tropics can be used. If the potential growth period is longer, then a number of perennials and biannual species are potential candidates, such as red clover (*Trifolium pratense* L.), sweet clover (*Melilotus alba* Medikus and *officinalis* Lam.), lespedeza (*Lespedeza stipulacea* Maxim), alfalfa (*Medicago sativa* L.), and others. If grown as a winter cover crop, hairy vetch and the nonlegume rye (*Secale cereale* L.) usually have sufficient winter-hardiness to survive. For milder areas (southern United States), crimson clover is also a good winter cover crop.

Data from a large number of green-manure field experiments show a grain yield increase for rice equivalent to 50 to 120 kg N fertilizer ha^{-1} or even more depending upon the green-manure biomass incorporated and its total nitrogen content (Goswami et al., 1988; John et al., 1989a; Singh et al., 1991). Use of green manures in temperate regions was summarized recently by Power (1987).

Little work has been done for estimating the amounts of N fixed by naturally occurring legumes, which are widely distributed as herbs in grasslands, bushes, and trees in savannah and trees and creepers in tropical forests. Orchard and Darb (1956) reported that a plantation of *Acacia mollisima* fixed as much as 270 kg N ha^{-1} yr^{-1} . By fixing atmospheric nitrogen, legumes provide stability to natural ecosystems.

8.7.2. Nitrogen Fixation by Blue-Green Algae (Cyanobacteria)

Blue-green algae may contribute 25 to 30 kg N ha^{-1} per cropping season, depending on ecological conditions (Venkataraman, 1979). However, Watanabe et al. (1977) measured C_2H_2 reduction before and after removing cyanobacterial growth from the rice field and concluded that the nitrogenase activity could account for a daily input of approximately 0.5 kg N ha^{-1} .

8.7.3. Azolla-Anabaena Systems

The Art of Feeding the People, a book on agricultural techniques written in 540 A.D. by Jia Ssu Hsieh, describes the cultivation and use of *Azolla* in

rice fields in China (Chu, 1979), indicating that *Azolla* has been used in rice fields in China since ancient times. International interest in *Azolla-anabaena* systems for meeting a part of the nitrogen requirement of rice is rather recent. The ecosystem requirements for *Azolla* include free-floating water, sufficient light, and temperature around 15°C. The most favorable temperature for the growth of *A. pinnata* is 16 to 17°C; much of the *Azolla* may die when the temperature rises to 20 to 24°C (Becking, 1979). The inability of *Azolla* to grow under high temperatures is a major barrier in using *Azolla-Anabaena* systems for supplying nitrogen to rice in many developing countries in Asia and Africa. However, when the temperature during the two-month period before rice planting does not rise above 30°C, it should be possible to use *Azolla* for this purpose.

The major nutrient requirement for *Azolla* is phosphate (10 to 25 kg P₂O₅ ha⁻¹). The addition of potassium also helps in the growth of *Azolla*. *Azolla* grows best in soils having pH between 5.5 and 7 (Singh, 1979), although some growth is reported even at pH 10. Acidic soils (pH 3.0 to 3.5) do not permit the growth of *Azolla*, and the inoculum dies.

Although laboratory estimates of N₂-fixation by *Azolla* could be as high as 335 to 670 kg N ha⁻¹ (Becking, 1979), field data normally suggest an N₂-fixation equaling a basal N fertilization of 30 to 40 kg N ha⁻¹.

8.7.4. Nonphotosynthetic Bacteria

The nitrogen-fixing power of nonphotosynthetic bacteria has been known for decades, and there is a fairly long list of species capable of this process (LaRue, 1977). The amount of nitrogen fixed by these bacteria is generally relatively small, and therefore there has been little interest in this topic. However, with the energy crisis in recent years, there is renewed interest in this avenue of nitrogen fixation.

8.7.5. Nodule-Forming Nonlegumes

Most nodulating nonleguminous plants with the capacity of fixing nitrogen are woody, and therefore their economic application is generally restricted to forestry and the general ecology of a region. Nevertheless, they do play an important role in overall human welfare. These associations have been recently discussed in detail by Becking (1977).

8.7.6. Nonsymbiotic N₂-Fixation

In addition to symbiotic N₂-fixation, nitrogen is also fixed in soil by nonsymbiotic bacteria *Azotobacter* spp. (aerobic) and *Clostridium* spp. (anaerobic). Available estimates suggest that 10 to 15 kg N ha⁻¹ yr⁻¹ is fixed by nonsymbiotic N₂-fixing bacteria. Cultures of these organisms have been successfully used in

Soviet agriculture, but the United States experience has not been very encouraging. Nevertheless, there is an interest in the use of cultures of *Azotobacter* spp. in developing countries (Thomas, 1993).

Other bacterial species (*Beijerinckia*) that fix atmospheric N inhabit the surfaces of a number of tropical plants and are in tropical soils (Becking, 1961). Dobereiner et al. (1972) reported nitrogen fixation by a *Paspalum notatum* - *Azotobacter paspali* association. In such an associative system no nodules are produced, but in some cases bacteria live underneath a mucilaginous sheath on the root surface. Dobereiner et al. (1972) suggested fixation of about 90 kg N ha⁻¹ for a *P. notatum* – *A. paspali* association. Later they reported the occurrence of a nitrogen fixing *Spirillum lipoferum* on the roots of the grass *Digitaria decumbens* (Dobereiner and Day, 1976). The amount of N fixed by associative systems is considered lesser than that for *Rhizobia*.

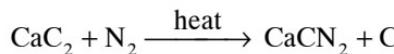
8.8. NITROGEN FERTILIZERS OR INDUSTRIAL NITROGEN FIXATION

Essentially all nitrogen fertilizers are produced from ammonia gas. Exceptions are small amounts of naturally occurring guano (bird droppings from South America) and sodium nitrate deposits. Over 90 million megagrams (Mg) of nitrogen are commercially fixed each year worldwide for use as fertilizers.

There are three methods by which atmospheric elemental nitrogen can be converted into a chemical form that can be directly used as a chemical fertilizer or can be used for making a chemical fertilizer. These methods or processes are (1) the cyanamide process, (2) the arc process of nitric acid synthesis, and (3) the Haber-Bosch ammonia synthesis process. A brief discussion on these follows.

8.8.1. Cyanamide Process

This process was developed by Frank and Caro in Germany in 1898 and involves passing purified nitrogen gas over calcium carbide kept at 1100°C.

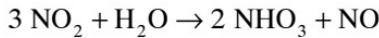
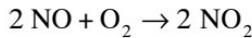
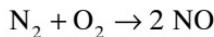


This process is used only on a very limited scale in Germany and other European countries, often for purposes other than making chemical fertilizers. Calcium cyanamide, when used as a fertilizer, has some toxic effects on crop plants, and application is generally recommended 4 to 6 weeks before sowing of a crop. Calcium cyanamide has also been used as a herbicide.

8.8.2. Arc Process

This process involves passing elemental nitrogen and oxygen through an arc that is expanded in an electromagnet to increase the contact with gases.

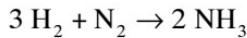
In nature, lightning also accomplishes this process and therefore is a source of nitrates in rain. The reactions are



This process can be used where electrical power is inexpensive.

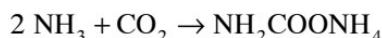
8.8.3. Haber-Bosch Process (Ammonia Synthesis)

Ammonia synthesis by the Haber-Bosch process is one of the few, most significant, scientific discoveries of the early twentieth century, and it led to Haber receiving a Nobel prize for this invention. Ammonia synthesis is based on the reaction of N₂ and H₂ in the presence of a catalyst, the main component of which is magnetite (Fe₃O₄), and at temperatures up to 1200°C. The pressure required varies from 200 to 1000 atm. The basic reaction is



While N₂ is obtained from the elemental atmospheric N, the source of H₂ is natural gas, naptha, fuel oil, and coal; the first three are products of the petroleum industry. Natural gas is by far the most important feed stock used for ammonia production. Where electrical power is inexpensive, H₂ can also be obtained by the electrolysis of water.

The anhydrous ammonia produced by this process can be used as such as a fertilizer (comprising 41.8% of total N consumed in the United States in 1990), or it can be reacted with nitric, sulfuric, and phosphoric acids to make ammonium nitrate, ammonium sulfate, and ammonium phosphate, all of which are important fertilizers. In the United States anhydrous ammonia is often delivered to farm communities by underground pipelines, resulting in a very inexpensive fertilizer material costing half as much as most other sources. Furthermore, anhydrous ammonia when reacted with carbon dioxide yields urea, which is an important N source in many Asian countries, as well as elsewhere in the world. The reactions are



(Urea)

Urea and ammonium nitrate can also be dissolved to make nitrogen fertilizer solutions, notably UAN, which is also used widely. UAN is often the fertilizer

Table 8.7 General Composition of Some Common N and NP Fertilizers

Fertilizer	N	P ₂ O ₅	CaO	MgO	S
N Fertilizers					
Ammonium sulfate	21	—	—	—	24
Anhydrous ammonia	82	—	—	—	—
Ammonium chloride ^a	25–26	—	—	—	—
Ammonium nitrate-sulfate	30	—	—	—	5–7
Ammonium nitrate with lime (ANL)/CAN ^b	20.5	—	10	7	—
Calcium nitrate	15	—	34	—	—
Calcium cyanamide	22	—	54	—	0.2
Sodium nitrate	16	—	—	—	—
Urea	45–46	—	—	—	—
Urea-sulfate	30–40	—	—	—	6–11
Urea-sulfur	30–40	—	—	—	10–20
Urea-ammonium nitrate (solution)	28–32	—	—	—	—
NP Fertilizers					
Ammoniated ordinary superphosphate	4	16	23	0.5	10
Monoammonium phosphate	11	48–55	2	0.5	1–3
Diammonium phosphate	18–21	46–54	—	—	—
Ammonium phosphate-sulfate	13–16	20–39	—	—	3–14
Ammonium polyphosphate solution	10–11	34–37	—	—	—
Urea-ammonium phosphate	21–38	13–42	—	—	—
Urea-phosphate	17	43–44	—	—	—

^a 66% chloride.

^b Calcium ammonium nitrate in India.

From Tisdale et al., 1993. *Soil Fertility and Fertilizers*, 5th ed., p. 156. With permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

of choice to mix with liquid P and K sources for use as a preplant starter fertilizer, and also for injection into sprinkler systems for use in fertigation.

A list of commonly used nitrogen fertilizers is provided in Table 8.7.

8.9. EFFICIENT NITROGEN MANAGEMENT

8.9.1. Recovery of Fertilizer Nitrogen

Recovery of fertilizer nitrogen is calculated as the fraction of fertilizer N applied that is removed in the harvested crop. Recovery values often vary from

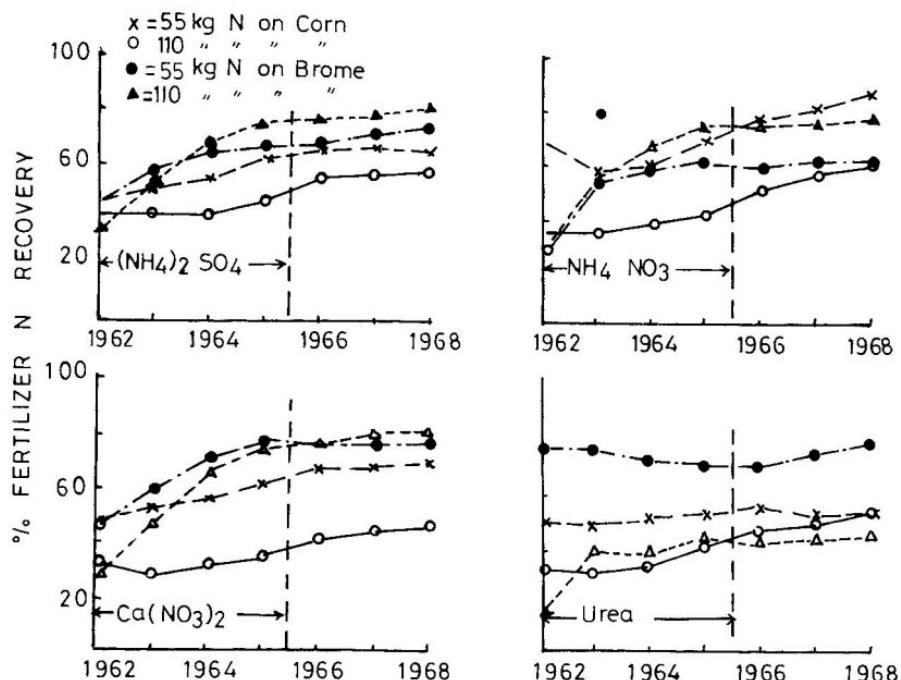


Figure 8.9. Fertilizer N recovery in plant tops from various N sources.
 (From Power et al., 1973. Agron. J. 65:765–768. With permission of SSSA.)

20 to 80% depending upon crop, amount of N, source of N, soil, frequency and amount of precipitation, and method used to calculate recovery. It is generally determined by the difference method using the expression:

$$\% \text{ recovery} = (\text{Nf} \pm \text{Nck}) / \text{Nap} \times 100$$

when Nf and Nck refer to N uptake in kg ha^{-1} in fertilized and check (no fertilizer) plots, respectively, and Nap is the amount of nitrogen applied in kg ha^{-1} . Since the amount of N applied may affect the quantity of native N released by soil (priming effect), this kind of recovery is referred to as apparent recovery. In a field experiment at Mandan, North Dakota (Power et al., 1973), N was applied to corn or bromegrass (*Bromus inermis* L.) at 55 or 110 kg N ha^{-1} for 4 consecutive years (1962 to 1965), and barley was grown for the following 3 years (1966 to 1968) without fertilizer. Data on apparent recovery of N are shown in Figure 8.9. Fertilizer N recovery was greater with bromegrass than with corn, due to a better root system and greater biomass for bromegrass. Also, recovery was greater with 55 kg N ha^{-1} than for 110 kg N ha^{-1} . Final recoveries, including residual N taken up by barley, ranged from 45 to 55% at 110 kg N ha^{-1} applied to corn to about 88% at 110 kg N ha^{-1} applied to bromegrass. At 110 kg N ha^{-1} ammonium sulfate and ammonium nitrate com-

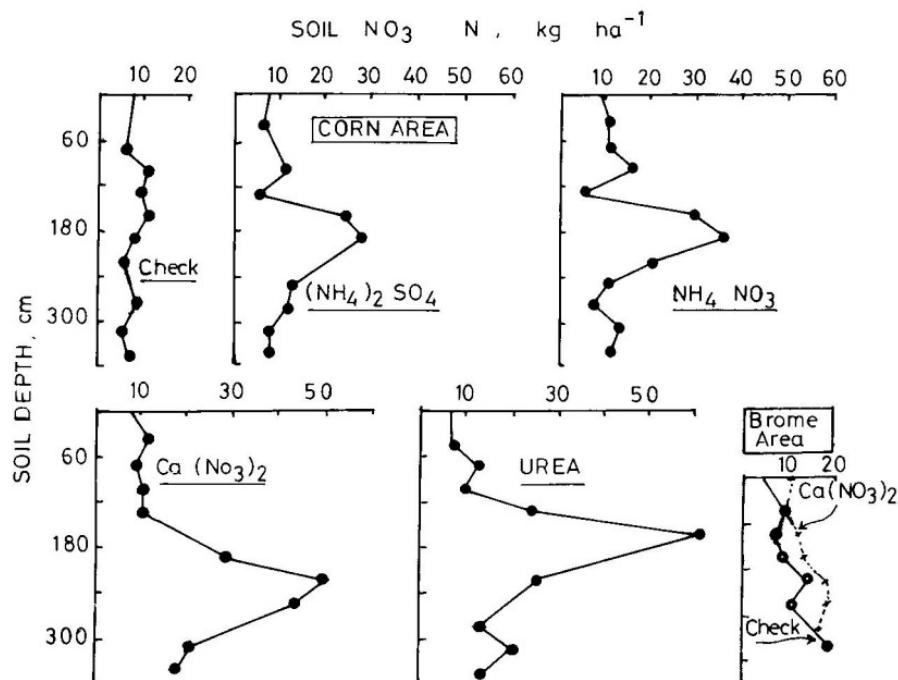


Figure 8.10. Soil nitrate-N distribution with depth after residual growth and N-uptake responses were complete (0 and 111 kg N/ha). (From Power et al., 1973. Agron. J. 65:765–768. With permission of SSSA.)

pared well and gave higher recovery than calcium nitrate and urea; this may have been due to more ammonia volatilization and/or leaching of nitrates for the latter two fertilizers (Figure 8.10). Similarly, the recovery of N applied to winter wheat was reported as 26 to 45% (Muchova and Apltauer, 1983; Janzen, et al., 1990) and 37 to 52% for spring wheat (Tandon, 1980). In recent years a large number of experiments have been conducted with ¹⁵N-enriched or -depleted fertilizer material, and data on ¹⁵N uptake permit the determination of direct recovery of the ¹⁵N applied. On coarse-textured alkaline (pH 7.7 to 7.9) soils of Punjab, India, ¹⁵N recovery by spring wheat was 65% with potassium nitrate and 33 to 44% with urea (Katyal et al., 1987). In a recent study in Nebraska (Francis et al., 1993) corn was grown on a Wood River silt loam and received 75, 150, 225, and 300 kg N ha⁻¹ as ammonium nitrate. At maturity only 21.2 to 54.3% of N present in the corn came from fertilizer, and only 24.4. to 35.3% of applied N was recovered by the crop (probably more was taken up, but some was lost by NH₃ volatilization before maturity) (Table 8.8). Generally, the difference method gives recovery values somewhat greater than the isotopic method. This may be due to the isotopic method reducing uptake of nonisotopic soil nitrogen and to failure of the isotopic method to evaluate residual effects of treatment in previous years.

Table 8.8 Total Plant N, Percentage of Plant N Derived from Fertilizer (Ndff), and Percentage of Fertilizer N Recovered by Corn at Maturity on Wood River Silt Loam in Nebraska

Fertilizer N kg ha⁻¹	Total N uptake by		
	plant tops (kg ha⁻¹)	Ndff (%)	Fertilizer N recovered (%)
75	87.4	21.2	24.4
150	122	35.0	28.5
225	164	39.8	28.9
300	194	54.5	35.3

From Francis et al. 1993. Agron. J. 85:659–663. With permission of ASA.

Table 8.9 ¹⁵N Balance in Rice-Wheat, Corn-Wheat-Mungbean, and Wheat-Mungbean-Corn Rotations (% of Applied N)

kg N ha⁻¹ applied to 1st crop	Recovered by			Left in soil	Unaccounted N
	1st crop	2nd crop			
	Rice	Wheat			
60	35.4	4.1		16.7	43.8
120	31.2	4.6		25.6	38.6
	Corn	Wheat	Mungbean		
120	20.8	7.0	0.8	40.1	31.3
	Wheat	Mungbean	Corn		
90	45.3	2.5	1.5	48.2	2.5

From Goswami et al. (1988) and Subbiah et al. (1985).

The efficiency of fertilizer N in tropical and subtropical environments is very low (Prasad and DeDatta 1979). Data are available from a number of experiments using ¹⁵N. In a field experiment at the International Rice Research Institute, Manila, Philippines, 29 to 40% of applied urea N was taken up by rice grain and straw (John et al., 1989a). At the Indian Agricultural Research Institute, New Delhi, India, George and Prasad (1989) found that the recovery of applied urea N by rice was 31.0, 26.7, and 25.9% at 50, 100, and 150 kg N ha⁻¹, respectively. Goswami et al. (1988) reported that in the rice-wheat rotation (growing rice July to November and growing wheat November to April) recovery of 60 kg N ha⁻¹ applied to rice was 35.4% by rice and 4.1% by the succeeding wheat (Table 8.9). Subbiah et al. (1985) reported that, when 120 kg N ha⁻¹ was applied to maize in a single dressing, only 20.8% could be recovered. Recovery could be raised to 38.3% by application in three split doses. Wheat succeeding maize recovered only 7% of that applied to maize. Succeeding crops of green gram (mung beans), corn, and wheat in the same field over the next 4 years recovered only negligible amounts (Table 8.9). However, when 90 kg N ha⁻¹ was applied to wheat,

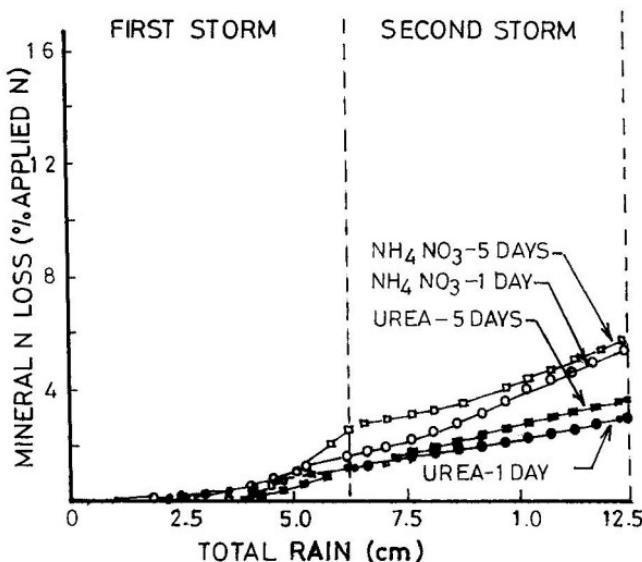


Figure 8.11. The effect of treatments on the amount of mineral nitrogen loss by runoff from fallow plots during five inches of simulated rain. Pelleted ammonium nitrate and urea applied to the surface of all plots at a rate of $44.8 \text{ kg N ha}^{-1}$ either 1 day or 5 days before rainfall. (From Moe et al., 1968. *Soil Sci.* 105:428–433. With permission of Williams & Wilkins.)

recovery was 46.3% by wheat, 2.5% by a succeeding green gram, and 1.5% by the maize that followed green gram. Thus efficiency of applied N was greater for wheat grown during the cold, dry period than for maize or rice grown during the warm, rainy season. Heavy rain and irrigation may have been responsible for N loss from the soil.

Data on N balance sheets (Table 8.9) show that about 16 to 48% of applied N may be retained or immobilized in the soil and 2.5 to 43.8% of applied N remained unaccounted (lost by various N loss mechanisms operating in soil). N loss mechanisms in soil therefore need to be carefully understood.

8.9.2. Nitrogen Loss Mechanisms

If not taken up by the crop plants or immobilized in soil, fertilizer N applied to crop fields may be lost by surface runoff, ammonia volatilization, nitrate leaching, denitrified as N_2 or N_2O , or lost as ammonia from foliage (Figure 8.1).

8.9.2.1. Surface Runoff

When heavy rains follow an application of fertilizer N, part may be lost by surface runoff, particularly with urea and nitrates, which are very soluble and

Table 8.10 Estimated Rates of Urea Hydrolysis in Soils and Overlying Paddy Water

Time interval (hr)	Rate of hydrolysis	
	Soil (mol s ⁻¹)	Water (mol s ⁻¹)
0–12	1×10^{-5}	2×10^{-7}
12–24	6×10^{-5}	2×10^{-6}
24–48	8×10^{-5}	4×10^{-6}

From Hongprayoon et al. 1991. Soil Sci. Soc. Am. J. 55:1130–1134. With permission of SSSA.

not retained by soil particles. Data from a simulated rain storm applying 12.5 cm of rain on a Lanesville silt loam in Indiana, having a 13% slope and a fragipan layer at 60 to 95 cm depth, are shown in Figure 8.11 (Moe et al., 1968). Losses were greater (5% of applied N) from ammonium nitrate than from urea (2 to 2.5%).

8.9.2.2. Urea Hydrolysis

When urea is used as a fertilizer and applied to a moist soil, it is first hydrolyzed to ammonium carbamate and then to ammonium carbonate by the enzyme “urease,” which is generally present in most soils. Ammonium carbonate readily degrades to NH₃ and O₂ gases. The pH of the soil in the vicinity of a urea prill may rise to 8.0 or above due to the formation of ammonium carbonate. This can result in loss of N by ammonia volatilization. Urea hydrolyzes fairly rapidly in soils.

The main site of urea hydrolysis in rice paddies is in the soil and not the floodwater (Delaune and Patrick, 1970). After 30 hours of incubation, 3 and 64% of the added urea was hydrolyzed in the floodwater and soil, respectively. In soil the rate of urea hydrolysis ranged from 1 to 8×10^{-5} mol s⁻¹, while hydrolysis rate in water varied from 2×10^{-7} to 4×10^{-6} mol s⁻¹, depending upon time interval (Hongprayoon et al., 1991) (Table 8.10). Depletion of O₂ in submerged soils retards urea hydrolysis. The order of hydrolysis rate is oxidized soil > reduced soil > floodwater.

Use of urease inhibitors such as phosphorodiamidate (PPD) and N (N-butyl) thiophosphoric triamide (NBPT) have been proposed as a strategy to reduce volatilization loss by retarding the hydrolysis of urea (Vlek et al., 1980). Because both urease inhibitors keep floodwater ammonia concentration low, they result in lesser ammonia volatilization (Buresh et al., 1988a). However, these urease inhibitors may have some phytotoxicity.

Amendment of urea with PPD or NBPT resulted in increased rice grain yield on a silty clay soil but not on a clay soil (Buresh et al., 1988b). Similar effects occurred for no-till corn (Schlegel et al., 1986).

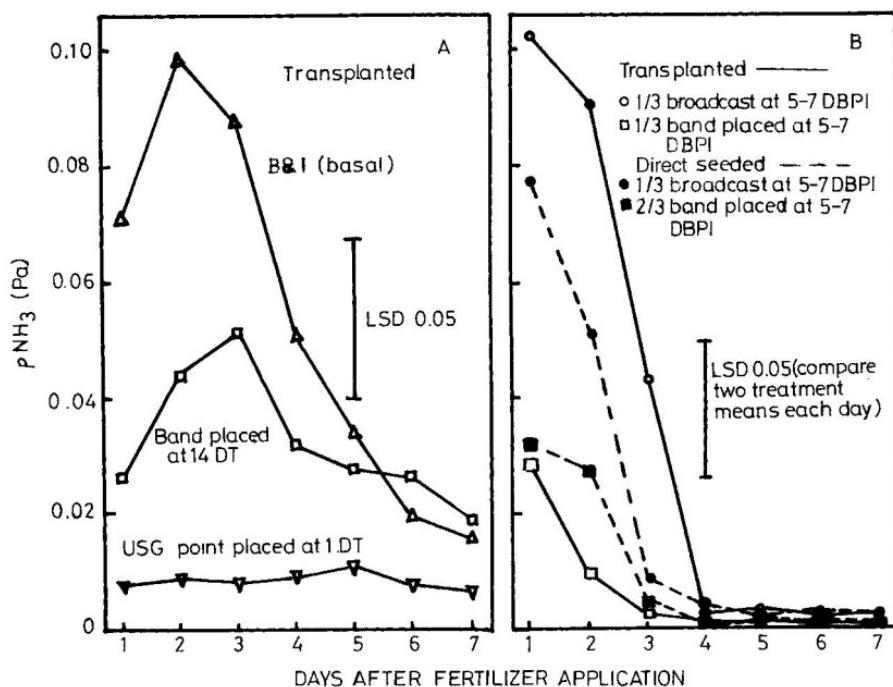


Figure 8.12. Partial pressure of NH_3 ($p\text{NH}_3$) in paddy floodwater at 1400 h, as affected by (A) method of basal N-fertilizer application and (B) N application 5–7 days before panicle initiation (DBPI), Munoz, Nueva Ecija, Philippines, 1987 dry season. *B&I*, broadcast and incorporated; *DT*, days after transplanting; *LSD*, least significant difference, *USG*, urea supergranules. (From Schnier et al., 1990. Biol. Fertil. Soils 10:89–96. With permission of Springer-Verlag.)

8.9.2.3. Ammonia Volatilization from Soils

Losses of N by ammonia volatilization after fertilizer application to crops range from 0 to 50% of the N applied. The factors that control ammonia volatilization loss include fertilizer form, method of application, soil pH, soil water content, cation exchange capacity of soil, wind velocity, air temperature, crop, and stage of crop growth. Ammonia loss under upland conditions is greatest from ammonium or ammonium-producing fertilizers applied on calcareous soils, where ammonium salts react with calcium carbonate to form precipitates of low solubility. Ammonia volatilization losses are very high when prilled urea is broadcast on a wet surface soil or on floodwater in rice paddies (Table 8.11) and can be considerably reduced by band or point placement of fertilizer urea or by use of coated urea or urea supergranules (USG — a modified urea form where the size of each granule may be a few mm to 1 cm in diameter) (Schnier et al., 1990) (Figure 8.12). Data in Figure 8.12

Table 8.11 Effect of Fertilizer and Water Management on Ammonia Volatilization Loss (% of Applied N) from Flooded Rice Fields

Urea applied kg N ha ⁻¹	Method of application	Mabitac silty clay	Calavun clay	Aguilar silty loam	San Marcelino loamy sand
53	B ₅ ^a	48	27	14	26
53	B ₅ & I	42	12	10	30
53	B _o & I	11	11	4	14
80	B ₅	56	23	10	36
80	B ₅ & I	43	12	10	26
80	B _o & I	7	16	5	10
LSD (p 0.05)		8	11	5	10

^a B₅ — basal dressing broadcast into 5 cm deep floodwater 10 days after transplanting. I — incorporated into soil by rotary harrow; B_o — basal dressing broadcast onto soil without surface water and incorporated into soil by rotary harrow; water returned to a depth of 5 cm 2 days after urea application.

From Freney et al. 1990. Biol. Fert. Soils 9:31–36. With permission of Springer-Verlag.

also show higher ammonia concentration in floodwater when urea was broadcast and incorporated than when it was band placed. Ammonia volatilization losses from rice fields range from 7 to 48% of the quantity of fertilizer N applied, depending upon the dose of N, its method of application, and soil characteristics (Freney et al., 1990). Losses were greater when urea was applied in 5 cm of standing water than when applied to a saturated soil. Incorporation of urea into the soil reduced ammonia volatilization loss.

Fertilizer applications to grazed pastures, which probably are one of the main sources of atmospheric NH₃, can result in large losses of ammonia, particularly if the applied urea falls on a urine patch. Losses by ammonia volatilization from urine-affected and unaffected soils were 27% and 7% of the applied N, respectively (Black et al., 1984).

Legume green manures, often advocated as an N source in soil-conserving production systems, may be particularly vulnerable to volatile N loss. In greenhouse studies at Alberta, Canada, (Janzen and McGinn, 1991) as much as 14% of the N applied as field-grown lentil (*Lens culineris*) residues was volatilized within 14 days of application.

8.9.2.4. Nitrogen Losses from Plants

The total amount of N in the aboveground biomass (grain plus stover) reaches a maximum well before maturity, often followed by a subsequent decline. In perennial species much of this N is probably translocated and stored in roots as a reserve to initiate growth the next season. However, for annual species (including most grain crops) there is little evidence of appreciable translocation to roots. Postanthesis N losses from wheat ranged from 5.9 to 80 kg N ha⁻¹ (Daigger et al., 1976; Harper et al., 1987; Papkosta and Gagianas,

1991) due to ammonia volatilization from the aboveground biomass. In a recent study in Nebraska (Francis et al., 1993) postanthesis fertilizer N losses ranged from 45 to 81 kg N ha⁻¹ for irrigated corn. Although not measured directly, volatile NH₃ losses from aboveground plant material appeared to be the most plausible explanation for this plant loss of N. Patron et al. (1988) at Fort Collins, Colorado, measured actual ammonia loss and reported that spring wheat lost ammonia at a relatively low and fairly constant rate (60 to 120 mg NH₃-N m⁻² s⁻¹) during presenescence (before milk ripe stage), but at rates of 200 to 300 ng NH₃-N m⁻² s⁻¹ during final plant senescence. Presumably in well fertilized crops, translocation of N from vegetative to reproductive tissue may be inefficient, allowing NH₃ to escape through the stomata in the respiration stream.

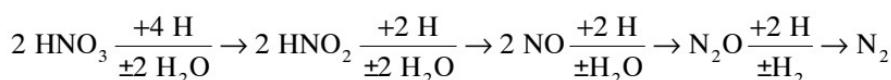
From a field study at Cuttack, India, and a pot-culture study at Fort Collins, Colorado, Mosier et al. (1990) suggested that young rice plants may facilitate the efflux of N₂ and N₂O from the soil to the atmosphere.

Thus the failure to include labeled N losses from aboveground plant biomass in N balance studies leads to overestimation of N losses from soil by direct ammonia volatilization, denitrification, and leaching.

8.9.2.5. Denitrification

Denitrification is the process by which nitrates are reduced to N₂ gas or various gaseous oxides of N. In soils most denitrification results from action of certain anaerobic and especially facultative microbes. Chemical denitrification can also occur, especially in acid soils. In microbial denitrification, nitrates serve as the oxygen source for the organisms. Soluble organic carbon compounds are used for microbial growth. For denitrification to occur, there are four requirements — anaerobic environment, presence of nitrates, presence of soluble carbons, and presence of denitrifying organisms.

When soils become submerged as in rice paddies or under heavy rainfall or irrigation under upland conditions, oxygen is excluded and anaerobic decomposition takes place. Plowing under a green manure crop can sometimes result in such a flush of microbial activity that soil O₂ supply is temporarily depleted to the extent that denitrification can occur. Some anaerobic organisms that belong to the genera *Pseudomonas*, *Bacillus*, *Chromobacterium*, and *Thiobacillus* (Table 8.12) can obtain their oxygen from nitrates and nitrites and release N₂ and N₂O. The most probable biochemical pathway is shown below:



Because of the release of N₂O (a greenhouse gas) and its involvement in ozone depletion, the process of denitrification has received considerable attention.

Table 8.12 Taxonomy of Denitrifying Microorganisms^a

Organism	Comments
<i>Achromobacter liquefaciens</i>	Oxidizes CH ₄ with NO ₃ ⁻
<i>Alcaligenes</i> sp.	Oxidizes CH ₄ with NO ₃ ⁻
<i>Bacillus</i>	Many species known to denitrify
<i>Chromobacterium</i>	
<i>Corynebacterium nephridii</i>	Produces only NO and N ₂ O
<i>Flursarium</i> spp.	Two species of this fungus reduce NO ₂ ⁻ (but not NO ₃ ⁻) to N ₂ O
<i>Halobacterium</i>	—
<i>Hydrogenomonas</i> spp. (= <i>Alkaliningenes</i> sp.)	—
<i>Hypomicrobium</i> sp.	Oxidizes methanol with NO ₃ ⁻
<i>Micrococcus denitrificans</i>	Chemolithotroph; oxidizes H ₂
<i>Moraxella</i>	—
<i>Propionibacterium</i>	—
<i>Pseudomonas</i> spp.	Many well-known denitrifying species
<i>Spirillum</i>	—
<i>Thiobacillus</i> spp.	Chemolithotrophs; oxidize S and S ₂ O ₃ ²⁻ with NO ₃ ⁻
<i>Veillonella alcalescens</i>	Strict anaerobe; both assimilatory and dissimilatory NO ₃ ⁻ reduction
<i>Xanthomonas</i>	—

^a Not all species within a genus may be capable of denitrification.

From Brezonik. 1977. Progress in Water Tech. 8:373–392. With kind permission from Elsevier Science Ltd., Kidlington, U.K.

The ratio of N₂ to N₂O and other oxides produced by denitrification depends on many environmental factors. Generally, however, the more anaerobic the environment, the greater the N₂ production.

Estimates of N losses by denitrification vary from 3 to 62% of applied N in arable soils. Losses were greatest from rice paddies. It may be mentioned that these values are arrived at by subtracting ammonia volatilization losses from the unaccounted ¹⁵N. The actual recovery of (N₂ + N₂O)-¹⁵N was only 0.1% of the applied urea in the study of DeDatta et al. (1991) and only 0.51% of the applied N in the study by John et al. (1989b) under field conditions. Consequently, the tremendous dilution of the isotope that occurs creates a large error in their measurements. Field measurement techniques of N₂ and N₂O therefore need to be improved. Also, N losses from the aboveground portion of the plant must be accounted for.

While denitrification in soil is primarily controlled by three primary or proximal factors (oxygen, nitrate, and carbon), these primary factors are affected by several physical and biological factors (distal factors). Thus it usually becomes necessary to focus on distal rather than proximal factors as

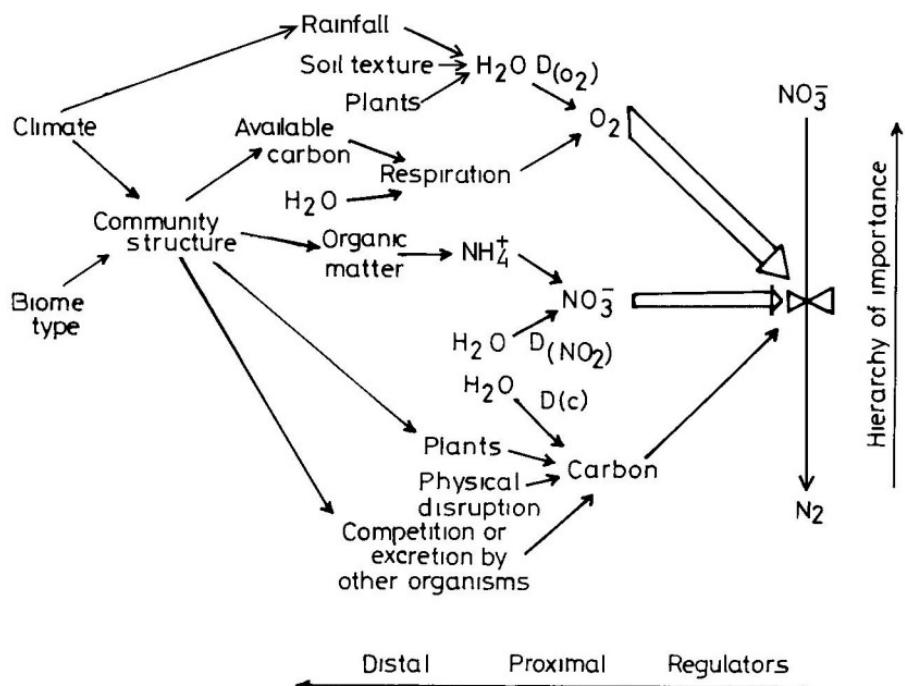


Figure 8.13. Relationship between proximal and distant controlling factors of denitrification. (From Tiedje, 1987. *Environmental Microbiology of Anaerobes*, Zehnder, A.J.B., Ed. With permission of John Wiley & Sons.)

controllers of denitrification (Groftman et al., 1988). The relationship between proximal and distal factors controlling denitrification is shown in Figure 8.13, while Figure 8.14 shows how the controlling factors change as the scale of investigation increases. Effects of primary factors on denitrification are briefly discussed. As already pointed out, an anaerobic condition is the basic requirement for denitrification to proceed. Therefore as oxygen concentration decreases, denitrification increases (Table 8.13). Because water and air comprise the soil pore volume, oxygen content decreases as water content increases and vice versa. The effect of increasing % water filled space on denitrification is seen in Figure 8.2.

A source of energy (carbon) is essential for denitrification. Consequently, denitrification generally increases with an increase in water-soluble, as well as with mineralizable, soil organic C.

In addition to oxygen, nitrate, and carbon, soil pH also influences the rate of denitrification. Since bacterial activity is generally low below pH 5, denitrification losses are very low in soils having pH 4 or less (Bremner and Shaw, 1958). Denitrification is most rapid at pH values 6 to 8.

Soil temperatures most suited to denitrification are 25 to 60°C; it is slow at lower temperatures and may be inhibited at temperatures above 60°C (Tisdale et al., 1985). An example of the effect of some distal factors (soil texture

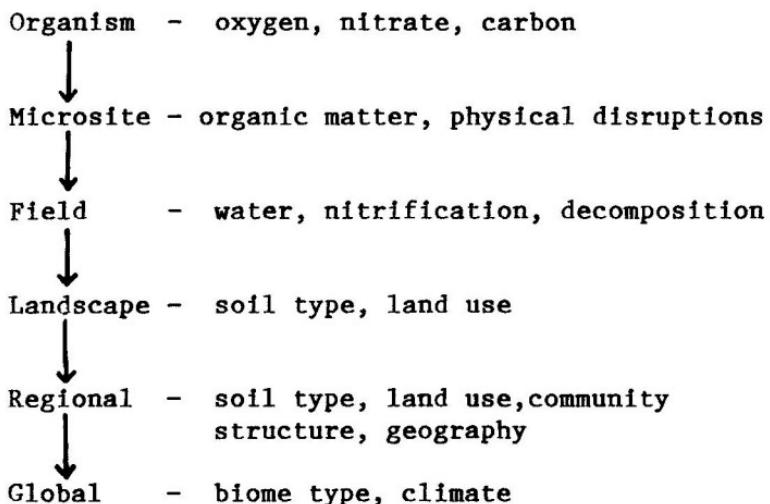


Figure 8.14. Factors controlling denitrification at different levels of investigation. (From Tiedje, 1987. *Environmental Microbiology of Anaerobes*, Zehnder, A.J.B., Ed. With permission of John Wiley & Sons.)

Table 8.13 Nitrate Uptake by a Plant (*Hordeum vulgare*) and Reduction by a Denitrifier (*Pseudomonas fluorescens*) at Different Oxygen Concentrations

Oxygen level (% v/v)	Denitrification ($\mu\text{g NO}_3^-$ -N mg^{-1} biomass h^{-1})	Plant uptake ($\mu\text{g NO}_3^-$ -N mg^{-1} biomass h^{-1})
20	0	1.85
10	0	1.15
5	0	0.52
1	0	0
0.05	0	0
0.01	0.15	0
0	3.5	0

From Wilson, R.J.R., Editor. 1988. *Advances in Nitrogen Cycling in Agricultural Ecosystems*. With permission of C.A.B. International.

and drainage) is given by data in **Table 8.14**. Denitrification loss was greatest in heavy (clay loam) soil. Also the increase in denitrification due to impoverished drainage was greater in clay loam than in loam soils and was least in sandy loam soil.

8.9.2.6. Leaching

Amount and intensity of rainfall, quantity and frequency of irrigation, evaporation rate, temperature effects, soil properties (particularly, texture and

Table 8.14 Annual N Loss Due to Denitrification as Affected by Denitrification, Soil Drainage, and Soil Texture for Forested Soils in Michigan

Soil	Denitrification N loss (kg N ha ⁻¹ yr ⁻¹)
Sand loam	
Well drained	0.6
Somewhat poorly drained	0.8
Poorly drained	0.5
Loam	
Well drained	10
Somewhat poorly drained	11
Poorly drained	24
Clay loam	
Well drained	18
Somewhat poorly drained	17
Poorly drained	40

From Wilson, R.J.R., Ed. 1988. *Advances in Nitrogen Cycling in Agricultural Ecosystems*. With permission of C.A.B. International.

structure), the type of land use, cropping and tillage practices, and the amount and form of N applied interact in complex ways to determine the amount of nitrates leached through the effective root zone, vadose zone, and eventually into the underground water.

Nitrate leaching can be accelerated by preferential flow of water through worm or root channels and natural fissures and cracks in soils. This is especially evident in vertisols. A number of computer simulation models are now available to predict nitrate leaching rates. The Nitrate Leaching and Economic Analysis Package (NLEAP) is an excellent computer program for identifying situations or practices where leaching could be excessive (Shaffer et al., 1991).

Leaching of nitrate is likely to be greatest under bare fallow. A 10-year comparison of nitrate profiles under pasture, fallow wheat, and continuous fallow in western Canada (Rennie et al., 1976) revealed leaching losses of 0 (pasture), 500 (fallow wheat), and 1082 (continuous fallow) kg N ha⁻¹ to 3.6 m depth. Vegetation reduces nitrate leaching; perennials such as trees and grass are more effective than annual crops. The average leaching loss of N was 4 kg N ha⁻¹ yr⁻¹ from grassland and 23 kg N ha⁻¹ yr⁻¹ from cultivated soils in a United Kingdom experiment (Cooke, 1976).

In a 10-year study in Minnesota (Nelson and MacGregor, 1973) on a Webster loam, about 50% of applied fertilizer N was taken up by corn, and at higher fertilizer rates quite substantial amounts of nitrate were present after harvest in the 5.5-m soil profile (Figure 8.15). These data also show that removal of N by the crop changed little when the rate of N increased from

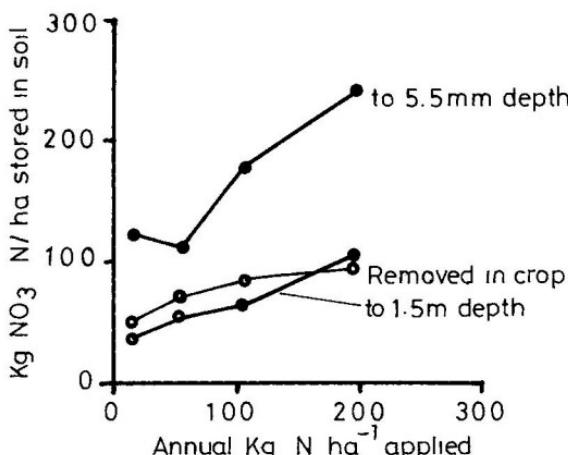


Figure 8.15. Relationship among fertilizer-N rate and amount of nitrate-N stored in soil 1.5 m and 5.5. m and nitrogen removed in crop. (From Nelson and MacGregor, 1973. *Soil Sci. Soc. Am. Proc.* 37:583–586. With permission of SSSA.)

100 to 200 kg N ha⁻¹. However, the increase in soil nitrate content (5.5-m depth) was considerable. These data clearly indicate that N leaching is greatly increased when fertilizer N rate exceeds crop needs. Thus, to control nitrate leaching into the groundwater, it is essential to develop reliable methods for predicting crop fertilizer needs.

The effects of land use and N fertilization on nitrate concentration in groundwater based on Western European experiences are summarized in Table 8.15. These data show that arable lands under vegetable cultivation contribute the most amount of nitrate to groundwater, and grasslands contribute the least. However, excessive leaching can even occur from grasslands when fertilizer N is applied at rates that exceed the need of the grass.

Gilliam (1991), based on an analysis of water samples over a 20-yr period in North Carolina, observed that drainage conditions prevailing in soil profiles affected nitrate concentration in soil water. In the lower coastal plain region, soils are poorly drained and have high organic matter content and high water tables. In these soils there is sufficient organic matter to provide an energy source for microorganisms so that denitrification occurs and nitrate concentrations are reduced (Figure 8.16A). On the other hand, in moderately well-drained soils little denitrification occurs and nitrate accumulation in groundwater is possible (Figure 8.16B). In these soils no nitrate was observed below 4 m because of the presence of an impermeable horizon. Water reaching these layers flows laterally to lower elevations, where it frequently enters a stream. Gilliam observed that these nitrates could be either utilized by plants along the way or lost by denitrification. No nitrate problem was recorded in the Upper Coastal Plains or Piedmont soils (Figure

**Table 8.15 Measured Site and Land-Use-Specific Nitrate N Input into the Groundwater
(Mean Concentration of the Annual Groundwater Recharge)**

Soil	Land use (crop rotation, N fertilizer)	Mean nitrate concentration (mg N L ⁻¹)
Sand	Arable land (cereal-sugarbeet/potatoes-cereal, $\approx 120 \text{ kg N ha}^{-1} \text{ yr}^{-1}$)	25–30
	Arable land (cereal-winter catch crops–sugarbeet/potatoes-cereal, $\approx 120 \text{ kg N ha}^{-1}$)	14–16
	Grassland (meadow, $\approx 250 \text{ kg N ha}^{-1} \text{ yr}^{-1}$)	3–7
	Grassland (intensively grazed pasture, $\approx 250 \text{ kg N ha}^{-1} \text{ yr}^{-1}$; = 2 livestock units ha^{-1} , ≈ 180 grazing days)	14–20
	Field cropping of vegetables, including special crops such as asparagus, tobacco (≈ 300 –600 kg N $\text{ha}^{-1} \text{ yr}^{-1}$)	34–70
	Woodland (coniferous tree stands)	2.5
	Woodland (alder tree stands)	10
Loess	Arable land (cereal-sugarbeet-cereal $\approx 150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$)	7–14

Adapted from Strelbel et al. (1989).

8.16C). In those situations Gilliam concluded that nitrate leaching to groundwater was possible only with high rates of fertilizer or manure application (Figure 8.16D).

Nitrate accumulation in groundwater can result not only from excess N fertilization, but can also occur when excessive rates of animal manures or other organic wastes are applied to soils. In addition, there are a number of geological strata (especially marine shales) that contain excessive nitrates and/or exchangeable ammonium, which, given the right conditions, can result in nitrates leaching into groundwater.

8.10. INCREASING N USE EFFICIENCY

Since fertilizer N efficiency is determined by the biomass yield and nitrogen uptake by a crop, all factors that affect biomass yield and nitrogen concentration in tissue will affect N use efficiency. These factors can be broadly classified into five groups, namely, soil factors, crop factors, environmental factors, agronomic practices, and fertilizer management. Some of these factors are enumerated below:

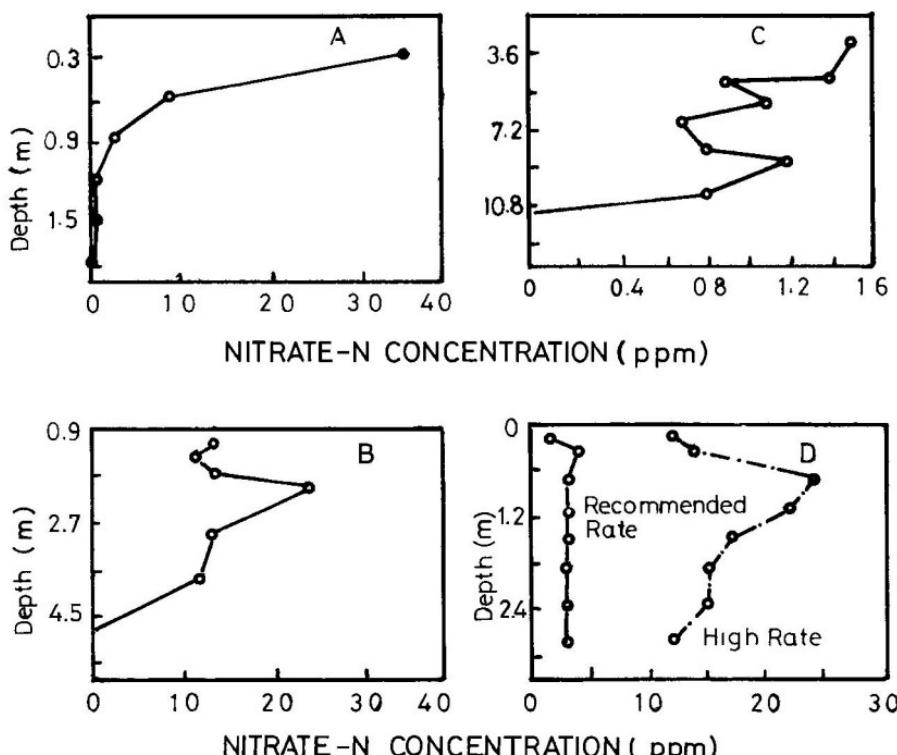


Figure 8.16. Typical nitrate-N profiles in North Carolina soils: A. Soil water NO₃-N in a cultivated, poorly drained, high water table, coastal plain soil. B. Soil water NO₃-N in a cultivated, moderately well drained, coastal plain soil with aquatard between 3 and 3.9 m. C. Soil nitrate-N profile of a cultivated Piedmont soil. D. Soil nitrate-N profile of an area of coastal Bermuda on a coastal plain soil receiving different rates of N. (Adapted from Gilliam, 1991. *Better Crops* 75:6–8. With permission.)

Soil factors

1. Initial fertility—very fertile soils give lower fertilizer N response.
2. Texture and structure—more leaching occurs in light, sandy soils.
3. pH, salinity/alkalinity—greater ammonia volatilization occurs in calcareous and alkaline soils.
4. Topography—surface runoff losses are greatest from upper topographic regions.
5. Drainage—poor drainage can lead to large denitrification losses.

Crop factors

1. Choice of crop (where more than one crop can be grown) and its yield potential (N uptake potential).

2. Choice of crop variety, its growth period, yield potential, and efficiency of nutrient utilization.
3. Resistance of the variety to diseases and pests, drought, and other stress factors.
4. Resistance of the crop variety to soil problems such as water logging, salinity, alkalinity, nutrient toxicities, etc.

Environmental factors

1. Rainfall and its distribution—large rains can lead to severe runoff and leaching losses.
2. Sunny days and sunshine hours, day length, heat units.
3. Occurrence and duration of frost, low night temperature.
4. Occurrence of thunderstorms, hail, tornadoes, wind damage.

Agronomic practices

1. Timely sowing—delays can reduce yield considerably.
2. Adequate plant population.
3. Water management—water-efficient irrigation practices in irrigated areas, water conservation practices for dryland conditions.
4. Adequate weed control.

Fertilizer management

1. Rate of application matched to crop needs.
2. Method of application to reduce nutrient losses.
3. Time of application matched to crop nutrient uptake pattern.
4. Source of N—modified urea materials, $\text{NH}_4^+/\text{NO}_3^-$ ratio, liquids.
5. Fertilizer amendments—nitrification and urease inhibitors, coatings.

The discussion on all the factors mentioned above is beyond the scope of this chapter and is restricted to fertilizer N management.

8.10.1. Rate of Nitrogen Application

Fertilizer nitrogen efficiency, in most crops, is generally greater at lower fertilization levels than at higher levels and decreases considerably when N rates increase beyond the optimum. For example, data in [Table 8.16](#) show that the increase in fertilizer N uptake by corn was greatly reduced beyond 100 kg N ha⁻¹. As a consequence, much more nitrate N was lost at rates above 100 kg N ha⁻¹ than below. Numerous data supporting this conclusion exist for most crops from all parts of the world.

8.10.2. Method of N Application

Since part of the N applied in ammonium or ammonium-producing fertilizers (urea) is lost through ammonia volatilization, particularly on calcareous and alkaline soils and in rice paddies, fertilizer placement at a few centimeters

Table 8.16 Nitrogen Balance for Microplots Treated with ^{15}N -Enriched Fertilizer

Fertilizer (kg N ha ⁻¹)	Crop uptake (% of initial N applied ^a)	Soil 0–2.4 m (% of initial N applied ^a)	Unaccounted for fertilizer (% of initial N applied ^a)
50	48 ± 1.1 (5.0) ^b	23.7 ± 7.5	28.3 ± 7.4
100	49.8 ± 3.1 (5.7)	20.0 ± 5.0	30.2 ± 7.0
150	53.1 ± 2.9 (5.9)	19.8 ± 8.1	27.1 ± 6.5

^a Mean ± the standard deviation.

^b Values in parentheses are included in the total and represent an estimate of the contribution of roots to total removed by plants based on roots comprising 15% of total plant dry weight at physiological maturity.

From Francis et al. 1993. Agron. J. 85:659–663. With permission of ASA.

depth is considered desirable and profitable. An example of the advantage of placement of N in rice fields has been shown in [Figure 8.12](#).

Soil injection is essential when anhydrous ammonia is used as a fertilizer. In a study in the United States (Stanley and Smith, 1956) loss of anhydrous ammonia was negligible when injected at a depth of 22.5 cm ([Figure 8.17](#)) irrespective of soil water content up to 18% (w/w). However, when injected at a depth of 7.5 cm, about 12% of the anhydrous ammonia was lost in a dry soil (2% w/w); loss was reduced to a little over 1% when soil water content increased to about 16%. Soil water dissolves ammonia and changes it to ammonium, which can be retained on the exchange complex of the soil.

8.10.3. Time of N Application

Because N is susceptible to loss from soil, it is desirable to apply N in small doses during the growth of the crop. Often fertilizer is applied in two or three split doses; the amounts at each application may be equally or differentially divided depending upon the rate of N, duration and need of the crop at different growth stages, and soil texture. Data from a field experiment on spring wheat conducted on light textured soils of Punjab (India) are shown in [Figure 8.18](#). On such soils a single basal application was desirable at 40 kg N ha⁻¹, two split doses when 80 to 120 kg N ha⁻¹ is applied (the most frequently recommended rate of N for wheat in India), and three split doses when 160 to 200 kg N ha⁻¹ is required.

Although split application of fertilizer N is most efficient, in regions such as the corn belt of the United States where N fertilizers are relatively cheap, many producers find it more profitable to apply a little extra N to counteract losses but to apply all the fertilizer in one preplant operation. However, under

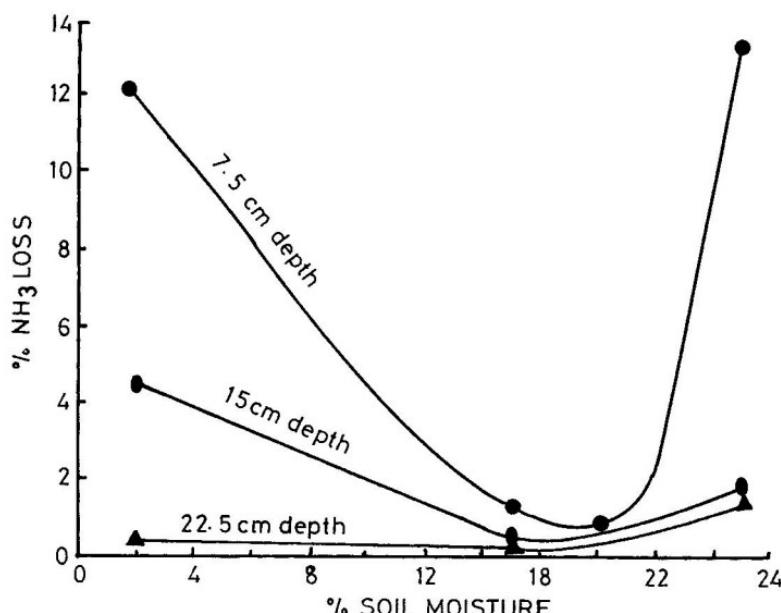


Figure 8.17. Losses of ammonia from a Putnam loam soil as influenced by depth of application and soil moisture. Anhydrous ammonia applied at the rate of 220 kg N ha⁻¹ (at 100-cm spacings). (From Stanley and Smith, 1956. *Soil Sci. Soc. Am. J.* 20:557–561. With permission of SSSA.)

certain conditions, this practice can result in excessive nitrate leaching and pollution of groundwater.

8.10.4. Nitrification Inhibitors

Since leaching and denitrification losses of fertilizer N take place only after ammonium or ammonium-producing fertilizers are nitrified, retarding the nitrification rate has been considered one way to reduce N losses and thereby increase N efficiency. By this means, fertilizer N is maintained primarily in the ammonium (nonleaching) form for several weeks until plant growth and N uptake rates increase to the extent that much of the nitrate formed is used immediately and nitrates do not accumulate in the soil. Nitrification inhibitors (NI) emerged as a group of agrochemicals with the development of N-serve or nitrapyrin (NP) (2-chloro-6 [trichloromethyl] pyridine). Since that time a large number of chemicals have been reported as NI, but only seven have been produced commercially; these are N-serve or NP; AM (2-amino-4-chloro-6 methyl pyridine); DCD (Dicyandiamide); ST (2-sulfanilamido thiazole); thiourea; Dwell or Ferrozole or Etridiazole (5-ethoxy-3-trichloromethyl-1,2,4,-thiadizole); and MBT (2 mercaptobenzothiazole). One natural product, namely, neem (*Azadirachta indica* Juss) seed extract (powder or cake), is also reported

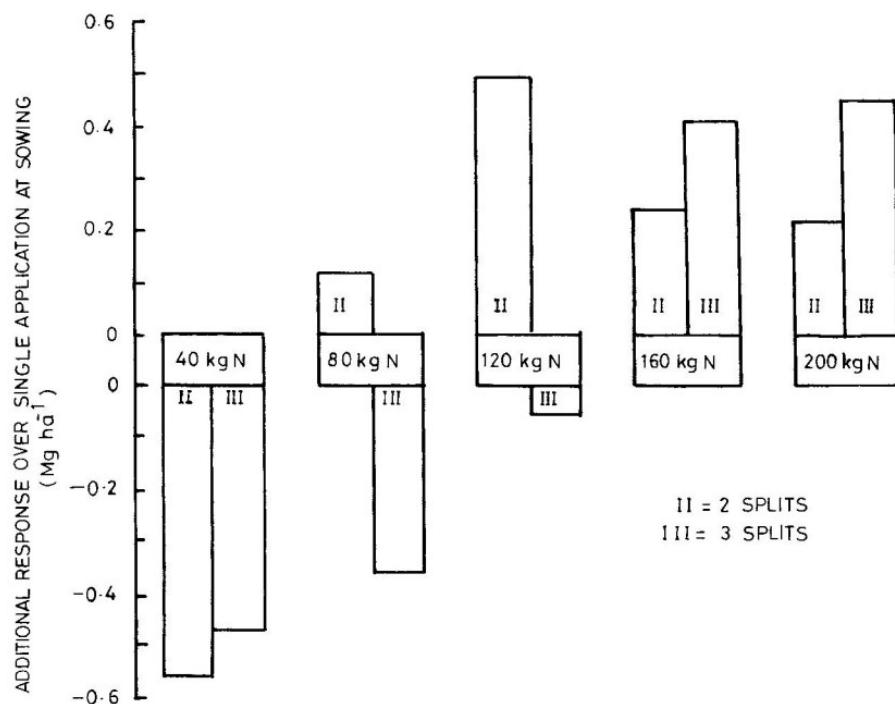


Figure 8.18. The effect of two or three split doses of N at increasing levels of N applied to wheat in a light textured soil. Means of 2 years. (From Sandhu and Gill, 1971. Indian J. Agric. Sci. 41:815–823.)

to have nitrification-inhibiting properties (Reddy and Prasad, 1975; Thomas and Prasad, 1982). Success with the use of NIIs under field conditions has been mixed; while some researchers found increased crop yield and N use efficiency with NIIs, others did not (Prasad and Power, 1995). In field experiments with rice conducted at the Indian Agricultural Research Institute, the NIIs, N-Serve, AM, ST, DCD, and neem cake showed a positive response (Reddy and Prasad, 1977; Sudhakara and Prasad, 1986). Prasad et al. (1981) reported that averaged over 6 years neem cake-coated urea (NCU) gave 0.4 Mg ha^{-1} more rice grain than prilled urea (PU). Furthermore, the residual effects resulted in 0.5 Mg ha^{-1} more grain in succeeding wheat. Similarly, field tests carried out in Japan (Nishihara and Tsunyoshi, 1968) showed an increase in rice yield with AM. Wells et al. (1989) summarized results with DCD on rice from Arkansas, California, Louisiana, Mississippi, and Texas and reported that DCD increased yields in both drill seeding and water-seeded, continuously flooding, rice culture. Use of DCD was advantageous only if the flood was delayed for more than 14 days after urea application.

With corn, the results of field experiments in the eastern corn belt of the United States showed that in 70% of the trials in Indiana there was an increase

in yield with NIs (Nelson and Huber, 1980). Results of experiments with DCD nitrappyrin in the north central United States indicated that the greatest benefit for NI use was obtained on coarse, textured soil. Results from experiments with NIs in the southeastern United States suggest limited benefits to corn due to high soil temperatures. Townsend and McRae (1980) from Nova Scotia, Canada, also observed that except on light, sandy soils, no yield advantage was gained with NP. In grain sorghum NP or Dwell applied with urea, anhydrous ammonia or urea ammonium nitrate solution did not increase yield nor improve efficiency of fertilizer N applied to grain sorghum during a period of 4 years, even with supplementary irrigation to promote leaching and/or denitrification (Westerman et al., 1981). Cotton is sensitive to DCD, and there was a tendency for cotton yields to decline with DCD.

8.10.5. Slow-Release N Fertilizers

One way of reducing N losses and increasing fertilizer use efficiency is to use fertilizer materials that release plant-available N slowly in the soil so that plants can utilize most before it is lost. Slow-release nitrogen fertilizers offer alternatives to the practices of split application and placement of N for increasing the efficiency of nitrogen applied to summer cereals (Prasad, 1982). These materials have drawn attention of agronomists, soil scientists, and fertilizer technologists the world over.

These materials can be broadly classified into two groups: (1) chemical compounds with inherently slow rates of dissolution, for example, urea-form, oxamide isobutylidene diurea (IBDU), and (2) urea and other nitrogen fertilizers provided with a coating that acts as a moisture barrier. Materials such as sulfur, shellac, plastics, and gypsum have been used.

Sulfur-Coated Urea (SCU). Of the slow-release fertilizers SCU, developed by the Tennessee Valley Authority, has been most widely tested. Due to slow release of N from SCU and to the localized acidifying effect of the sulfur, ammonia volatilization losses are usually reduced by using this material. SCU has been tested mostly for the rice crop. Engelstad et al. (1972), summarizing the results before 1972, observed that the response to SCU was generally good and superior to the response to urea in a single application and often exceeded yields for split applications of prilled urea applied at the same N rate.

Isobutylidene Diurea (IBDU). IBDU as a source of N has been the subject of considerable study in Japan, where it was developed (Hamamoto, 1986). This material gave 20% more rice than ammonium sulfate at equivalent N rates. It has also been evaluated in the United States (Hughes, 1976) and India (Rajale and Prasad, 1975). Release of N from IBDU depends upon soil pH and on fertilizer particle size. Hughes (1976) reported that N release from

IBDU was much more rapid in acid than in alkaline soils. He observed that 75% of N from IBDU was released after 10 weeks with a particle size of 0.6 to 0.7 mm, 58% in 21 weeks with 1.0 to 1.2 mm, and 50% in 32 weeks with 1.7 to 2.0-mm size particles.

Plastic-Coated Urea. In recent years, urea and other fertilizer materials have been encapsulated in decomposable polyvinylchloride or other plastics that are slowly decomposable to control release rate.

8.10.6. Urea Supergranules (USG)

Urea supergranules were developed based on the mudball technique followed in China for increasing the efficiency of fertilizer N. In the mudball technique, a small amount of fertilizer is placed in the center of a mudball by making a hole in the mudball and closing the hole after fertilizer injection. The mudballs are then dried and kept ready for use. Mudballs are placed deep in rice fields at an appropriate time. This is certainly a laborious and time-consuming process. Urea supergranules are aimed at overcoming this. Urea supergranules and briquettes can be made of different shapes and sizes. The 1-g size has generally been most tested. The deep placement of USG by hand or machine is an agronomically efficient, economically sound, and environmentally safe practice in the traditional transplanted rice growing areas, especially those that have nonpermeable soils. Studies over a period of 10 years at IARI in New Delhi (Prasad et al., 1989) showed that USG had a yield advantage over urea of 0.4 Mg ha^{-1} (10.7%). A large number of trials at research centers, as well as on farmer fields, have shown USG to be more efficient than prilled urea for rice on medium and heavy soils only (Kumar et al., 1989). In light, sandy soils the USGs have not been superior due to increased leaching (Katyal et al., 1988). For best results USG should be placed 4 to 5 cm below the soil surface (Singh et al., 1989). To some extent this requirement restricts acceptance because a low-cost applicator is not yet available.

8.11. NITROGEN AVAILABILITY INDICES

A nitrogen availability index is a quantitative value or a certain soil property (or group of properties) that presumably correlates with the amount of nitrogen made available to a crop during the growing season. Such indices may be used to predict nitrogen fertilization rate or other management practices. This topic was reviewed by Keeney (1982).

Total soil N and soil organic matter were the first indices used, and they are still used by some as an index of available soil N. Generally, however, total soil N by the Kjeldahl method is too costly and time consuming for routine soil testing. Nevertheless, soil organic matter can be determined quite rapidly and it is still widely used. In addition to total N and organic matter,

other popular indices are chemical extractants or hydrolysis agents such as 1 or 6 N $(\text{NH}_4)_2\text{SO}_4$ (Gallagher and Bartholomew, 1964), $\text{Ca}(\text{OH})_2$ (Prasad, 1965), 0.1 N $\text{Ba}(\text{OH})_2$ (Jenkinson, 1968), alkaline KMnO_4 (Stanford, 1978), 0.01 N CaCl_2 (Standford, 1968), and 1 N NaOH (Cornforth and Walmsley, 1971). An electroultrafiltration (EUF) procedure (a form of electrophoresis) is used in Germany to determine the fertilizer requirement for sugar beets (Nemeth, 1979). A number of biological tests have been proposed such as $\text{NO}_3\text{-N}$ liberated in 14 to 78 days of incubation (Gallagher and Batholomew, 1964); N mineralized in 14 to 112 days of incubation (Stanford and Smith, 1972); inorganic N released by autoclaving (Standford and DeMar, 1970); and anaerobic mineralization (Cornforth and Walmsley, 1971). None of the above soil tests has been universally accepted. The current thrust in the United States is on measurement of residual soil profile $\text{NO}_3\text{-N}$ (Stanford and Smith, 1972). Soil samples are taken soon after harvest or just before planting to a depth of 60 to 120 cm. This test is known as the preplant nitrate test (PPNT) (Fox and Piekielek, 1983). This method has met with success in North Dakota, Oklahoma, and Nebraska. The Nebraska interpretation employs an equation to calculate the fertilizer N requirement as a function of the yield goal, the crop N content, and a constant 56 kg ha^{-1} soil N addition.

In addition to or in place of PPNT, there is considerable effort to use PSNT (Pre-sidedress soil nitrate test) (Meisinger et al., 1992; Fox et al., 1992). Sampling of soil (30 cm depth) before sidedressing and analyzing for $\text{NO}_3\text{-N}$ is considered to provide a more reliable index of available soil N and is used for making a decision on the amount of N to be sidedressed. The major drawback is the short time (about 2 to 3 weeks) available for collecting the soil samples, analyzing for $\text{NO}_3\text{-N}$, deciding the rate of N to be applied, and then actually applying the fertilizer N. A more rapid approach is to determine the degree of N stress by measuring the chlorophyll content of corn leaves using a handheld chlorophyll meter (Schepers et al., 1992) or by remote sensing.

8.12. NITROGEN-DEFICIENCY SYMPTOMS

Nitrogen-deficiency symptoms are the most prevalent and easiest to identify. Young crop plants exhibit yellowish green foliage and stunted growth. In older plants there is yellowing or firing on the lower leaves, usually starting at leaf tips and margins ([Figure 8.19](#)). Ears are small, and the protein content in grain is low. Nitrogen deficiency is a major barrier to yield all over the world, particularly in developing countries. An effective integrated approach employing organic manures, biofertilizers, chemical fertilizers, nitrification inhibitors, and coated and long-persisting nitrogen fertilizers is the key to sustainable agriculture. Specific plans would differ from country to country and region to region because of differences in climates, soils, crops, labor supply, knowledge base, financial resources, and other reasons.



Figure 8.19. Nitrogen deficiency in corn (maize). Firing (or yellowing) of the midrib of older, lower levels of the plant (left), close-up of firing (right). (From *Corn Field Manual*, J.R. Simplot Company Minerals & Chemical Division, Pocatello, ID, ©1984. With permission.) See Plate 1 following p. 170.

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